THE ACTION OF HYDROGEN PEROXIDE ON CAOUTCHOUC.

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Owing possibly to the unattractive nature of the raw material, the chemistry of caoutchouc has not received the attention merited by the basis of such a large and important industry. Caoutchouc was known in the sixteenth century. In 1825 it was first used for proofing cloth, and in 1839 crude methods of vulcanisation were practised, yet it was not until 1860 that the chemical constitution of the substance and its derivatives aroused speculation.

Caoutchouc is a tough, elastic hydrocarbon, which forms extremely viscous colloidal solutions with a limited number of solvents such as ether, petroleum, benzene and its homologues, chloroform and carbon tetra-chloride. Treated with any of these solvents, caoutchouc first swells considerably, taking up a large quantity of the solvent, and a jelly is formed, this slowly merging into a viscous and apparently homogeneous solution.

The natural source of the hydrocarbon is the latex, or white watery emulsion obtained by making incisions in the bark of certain tropical and sub-tropical trees. This latex contains besides caoutchouc, a certain quantity of protein matter which acts as a protective colloid and renders the emulsion stable.

Coagulation of the latex is effected by the addition of small quantities of acetic acid, which removes the protein and neutralises/

neutralises the electric charges of the colloid particles. The resulting coagulum is then dried and prepared for manufacture by washing, rolling and bleaching with $NaHSO_3$.

As the product obtained by this method still contains a proportion of resin and protein matter, further purification for experimental purposes may be effected by extracting the shredded material with boiling acetone for a period of about 10 hours. For analytical purposes, caoutchouc is purified by dissolving in benzene, decanting the solution from the insoluble matter, and precipitating the hydro-carbon with alcohol.

Prepared in this manner, caoutchouc is a touch, elastic, transparent substance, which readily undergoes spontaneous oxidation.

As will be seen in the following pages, the chemistry of caoutchouc is closely linked with that of the under-mentioned hydrocarbons:-

Erythrene, divinyl, or buta - 1.3 diene $CH_2:CH.CH:CH_2$.

Isoprene or 2 methyl buta - 1.3 diene $CH_2:CMe.CH:CH_2$.

Piperylene or 1 methyl buta - 1.3 diene $CHMe:CH.CH:CH_2$.

Dipropylene or 2,3,dimethyl buta - 1.3 diene $CH_2:CMe.CMe:CH_2$.

1,1,4,4, Tetramethyl buta - 1.3 diene $C(Me)_2:CH.CH:C(Me)_2$.

Of these, isoprene and erythrene are the most important, the former being one of the products of the dry distillation of caoutchouc, whilst both, owing to their highly unsaturated character, readily polymerise to give bodies closely resembling natural caoutchouc.

The history of the chemistry of caoutchouc is meagre in that there are few series of researches of a consecutive character. This is due to the fact that with the exception of the diozonide, caoutchouc forms few compounds of definite composition, and most of these have failed to throw any light on its structure.

The earliest series of investigations was on the destructive distillation of caoutchouc, and, almost simultaneously, on the subsequent repolymerisation of the distillate to form more complex hydrocarbons.

That caoutchouc is a hydrocarbon had been established by the analyses of Berzelius, Faraday and Ure, and later, Gladstone and Hibbert, its empirical formula being C_5H_8. Since then, by analogy with the terpenes this formula has become $C_{10}H_{16}$, which possibly has proved a misfortune in that it led many chemists to try to express compounds as derivatives of $C_{10}H_{16}$ or some polymer of this, all apparently accepting caoutchouc as a polymerised terpene, and interpreting their analyses to suit.

By the destructive distillation of caoutchouc Greville Williams (Proc. Roy. Soc. 1860.10.516) obtained two main products, one boiling at 37-40° and the other at 170-180° after refractionation. The former was named isoprene and the latter, caoutchine, has since been identified as dipentene. Williams stated that the isoprene on standing in a stoppered bottle for a considerable time became "ozonised" and viscous. On distillation he was left with a tough white viscous mass, which on analysis was found to contain/

contain a certain proportion of oxygen. It seems certain that repolymerisation of the isoprene fraction had proceeded to some extent.

Five years later, stirred by a Government report on the perishing of gutta percha telegraph cables, Spiller examined the products obtained from perished caoutchouc (J.C.S.1865.18.44). Some waterproof packing sheet (unvulcanised) was thoroughly extracted with C_6H_6 and on evaporation a yellow resin, mixed with caoutchouc was obtained. This resin was purified by extraction with alochol and was found to be soluble in $CHCl_3$, methyl alochol, and in alkaline solutions, being reprecipitated by acids. It was insoluble in CS_2 and turpentine and sparingly soluble in ether. He collected further quantities and analysed it, obtaining values which corresponded roughly to $C_{10}H_{16}O_3$, or more closely to $C_{30}H_{48}O_{10}$. The author refrained from any speculations as to the nature of this oxy-compound. Bouchardat in 1875 published a paper "On the Synthesis of a Terpilene" (Compt.Rend.80.1446) in which he stated that isoprene heated in a sealed tube to 280° for 6 hours yielded a terpene oil, caoutchine or dipentene. Further work on isoprene appeared four years later in a paper "Action of HCl on Isoprene and the Reproduction of Rubber", (Compt.Rend.89.1117). He acted on isoprene with cold conc aqueous HCl and, after distillation, obtained a product which was elastic, swelled in ether and CS_2 and was insoluble in alcohol. These earlier investigators had/

had no tests such as the nitrosite, tetrabromide or diozonide whereby a true caoutchouc might be identified, and this has led later workers, notably Harries, to query many of these claims to have polymerised isopene to caoutchouc.

Bouchardat in this case actually tested his product by dry distillation and obtained products similar to those from natural caoutchouc.

This claim in particular has been disputed by Harries who could not repeat the experiment, but in his paper Harries speaks of gaseous HCl, whilst Bouchardat used conc. aqueous HCl.

Tilden in 1882 (Chem.News, 46. 220) and 1884 (J.C.S.45, 410) published papers on "Hydrocarbons of formula $(C_5H_8)_n$". He obtained isopene by passing turpentine through a red-hot tube, and after careful refractionation obtained it as a mobile liquid boiling at 34-35°, this apparently being a much purer substance than that used by previous workers. He stated that pure caoutchouc may be obtained from isoprene by the action of NOCl or conc HCl. In his second paper he polymerised the isoprene by means of heat and obtained dipentene and a thick oily polymeride which became tough and elastic on treatment with strong acids in the cold. This polymerisation of isoprene to dipentene was confirmed by Wallach (Ann.227,295) and two years later this worker discovered that isoprene exposed to sunlight in a sealed tube slowly polymerised to a tough elastic body insoluble in alcohol

(Ann./

(Ann.238,88). Some of Tilden's specimens of isoprene had been preserved since his work in 1886, and in 1892 he observed that these had become viscous and contained much gelatinous matter. (Chem.News.65,265.)

The liquid had a distinct acid reaction and, on pouring into alcohol, the gelatinous body coagulated to form a white insoluble substance closely resembling caoutchouc. He considered the acidity of the liquid to be due to formic or acetic acid produced by atmospheric oxidation.

Weber (J.Soc.Chem.Ind.1894,13,11) reviewed the spontaneous polymerisation of isoprene to rubber and suggested that rubber was a terpene or polyterpene $(C_5H_8)_n$ and three years later Ipatieff (J.Pr.Chem. ii. 55) elucidated the constitution of isoprene. Acting on it with HBr he obtained $CH_3.CMeBr.CH_2.CH_2Br$. as the chief product. From this he gave the structure of isoprene as $CH_2:CMe.CH:CH_2$. This, however, did not lead to any discussion as to the linking up of isoprene nuclei to form the caoutchouc molecule.

Very shortly afterwards Kondakow (J.Pr.Chem.64-109) noticed that polymerisation to caoutchouc-like bodies was not confined to isoprene alone. From dimethyl butadiene he obtained a white elastic substance which, though it swelled in C_6H_6, was insoluble in most of the usual caoutchouc solvents. This was the first of the many methyl-rubbers since obtained by polymerisation of the homologues of isoprene.

By/

By this time the synthetic production of caoutchouc or caoutchouc-like bodies (the absolute identity had not yet been established through lack of definite tests) may be said to have been firmly established. The necessary experimental conditions were still only vaguely known and the results could in no way be guaranteed. The facts, however, were known and continuous attention to conditions of experiment culminated in the Bayer Patents of 1909, for the production of caoutchouc by the hot polymerisation of isoprene. The glacial acetic acid process (~~Haines~~ Harries 1910) and the sodium process in which isoprene, and its homologues in presence of metallic Na polymerise to give a good yield of a workable product have now made large scale manufacture of synthetic rubber possible. The work of Tilden and Weber attracted new investigators who approached the subject from a different angle. They devoted their attack to the caoutchouc molecule itself, attempting to determine its structure and complexity by means of definite chemical derivatives and physical constants. An early investigation is found in the paper by Gladstone and Hibbert (T.Chem.Soc.1888,679) who sought to determine the unsaturation of the caoutchouc molecule in C_6H_6 solution by means of the refraction and dispersion equivalents. These figures were then verified by preparing chlorine and bromine addition products capable of being analysed. The results they obtained went to show that for each $C_{10}H_{16}$ group there were

3/

3 pairs of doubly linked carbons. Acting on caoutchouc in $CHCl_3$ with Cl_2, they found that addition and substitution took place simultaneously, and a product was obtained which gave an analysis $C_{10}H_{14}Cl_8$. The unsaturation was tested also with standard bromine solutions. Almost 4 atoms of bromine were taken up by each $C_{10}H_{16}$ group under ordinary conditions, but after prolonged action a product was obtained which gave on analysis $C_{10}H_{15}Br_5$, possibly by loss of HBr from $C_{10}H_{16}Br_6$. These results certainly seem to uphold the figures given by the refractive indices. Halogen and halogen acid compounds were also prepared by Weber (Ber.1900,33.779). With bromine he obtained the now well-known tetrabromide though his method seems to have resulted in other compounds being also produced, since his tetrabromide showed an appreciable and varying solubility in $CHCl_3$. Iodine gave a product $C_{20}H_{32}I_6$ whilst with moist HCl the dihydrochloride $C_{10}H_{16}.2HCl$ was obtained. On heating this dihydrochloride he seems to have obtained as sole product the mono-hydrochloride. Later work by Harries (Ann.1914,406-173) goes to show that the hydrochloride dissociated by heat in vacuo loses all but 1 molecule of HCl from $C_{30}H_{48}.6HCl$. The Nitrosite which has since played such an important part in the estimation and identification of caoutchouc was first described by Harries (Ber.1901,34,2991). Passing the purified gas, obtained by heating/

heating AS_2O_3 with HNO_3, into a petroleum solution of caoutchouc, he obtained a yellow flaky compound, soluble in ethylacetate and insoluble in ether. It was acidic, being soluble in alkaline solution and reprecipitated by the addition of acids. Analysis gave its composition as $C_{40}H_{62}O_{24}N_{10}$. Weber (Ber.1902,35,1947) performed similar experiments with nitrosyl chloride and nitrogen peroxide. With NOCl he obtained a stiff jelly which on standing decomposed to give apparently unchanged caoutchouc. Nitrogen peroxide, obtained by heating $Pb(NO_3)_2$ was passed into a C_6H_6 solution of caoutchouc. This yielded a yellow powder which was soluble in acetone and reprecipitated on addition of water. It was acidic in character forming salts with Na and Ag. Analysis gave the composition $C_{10}.H_{16}.O_4N_2$. This product however is the nitrosate and is quite distinct from Harries' nitrosite. At this time Dittmar was investigating the action of ~~conc.~~ HNO_3 on caoutchouc. He found (Ber.35,1401) that a vigorous action occurred, which yielded a yellow-red substance which could be precipitated from ethyl acetate by the addition of ether. It also was acidic in character and had the composition $C_{10}H_{12}O_6N_2$. This work was confirmed by Harries (Ber.35,3256) who also supplied further information about the nitrosite. The normal action of N_2O_3 on caoutchouc in C_6H_6 gave nitrosite (A) $(C_{10}H_{16}O_3N_2)_x$: with moist benzene and unwashed N_2O_3 he obtained nitrosite C a yellow powder $C_{20}H_{30}O_{14}N_{16}$. He also described a nitrosite

b/

b, obtained by the prolonged action of N_2O_3; it was acidic, had mol.wt.600, and composition $C_{20}H_{30}O_{16}N_6$, but shortly afterwards he corrected this, stating that nitroside b was an oxidation product obtained through the presence of Cl_2 and NOCl in his N_2O_3 which had been dried over $CaCl_2$. By this time it was becoming evident that the nitrosite was not going to yield much information about the actual caoutchouc molecule. The preparation of the compound was very susceptible to experimental conditions and, when prepared, the compound could only be subjected to ultimate analysis, the results of which varied greatly. Harries himself used many formulae apparently to describe the same compound, which he evidently regarded as being of a highly associated character. The compound obtained by Dittmar using conc. HNO_3 was identified by him (Monatsch.1904, 25.464) as either 3:6 or 5:6 dinitrodihydrocuminic acid, which indicated a considerable degradation of the original caoutchouc structure.

A paper by Sir W.Ramsay and his workers was published (J.Soc.Chem.Ind.21.1367) which covered the subject generally. Gutta percha was purified by precipitation from benzene by alcohol and subjected to ultimate analysis. This gave the composition as $(C_5H_8)_n$. On dry distilling, isoprene was obtained along with higher boiling fractions. With Br_2, the tetrabromide $C_{10}H_{16}Br_4$ was obtained. An ethereal solution of guttapercha was oxidised by atmospheric oxygen and/

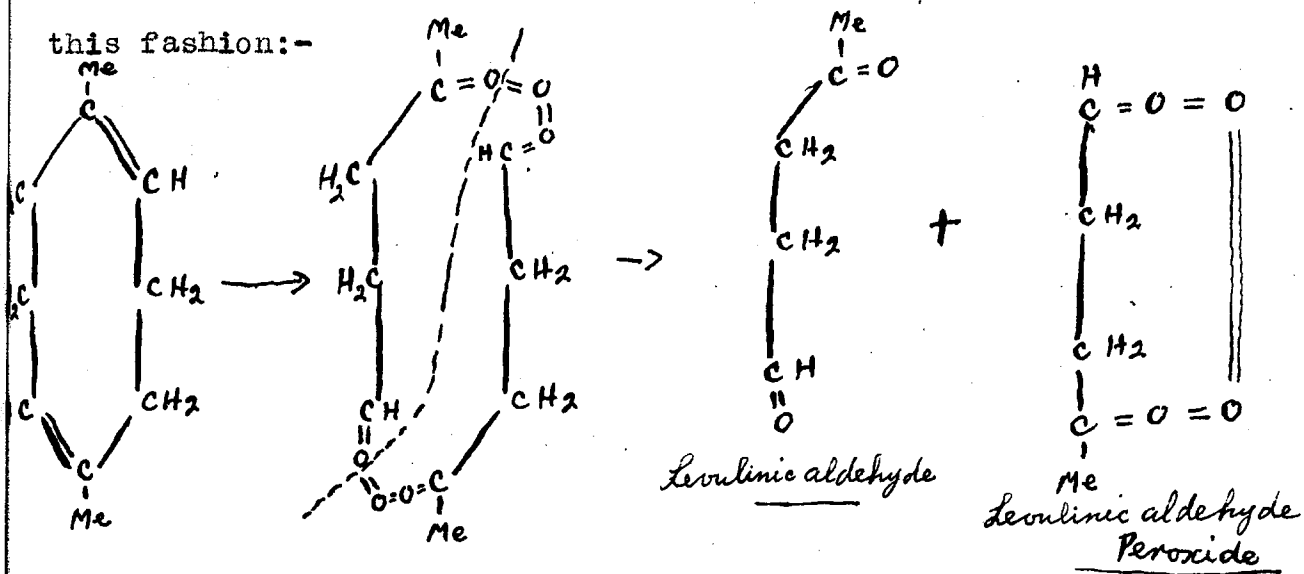
and a syrupy compound was obtained which was analysed and shown to be $C_{17}H_{26}O$. A similar experiment was carried out using toluene as the solvent, and the oxidation product in this case had the formula $C_{12}H_{24}O_4$.

In 1904 (Ber.37,2708) there appeared the first of Harries' brilliant researches which opened practically a new era in the chemistry of caoutchouc. Turning to the method which had previously fixed the constitution of oleic acid and other unsaturated bodies, he prepared the ozonide of caoutchouc by passing ozonised air into a cold $CHCl_3$ solution of the hydrocarbon. The ozonide was obtained as a vitreous mass and had a molecular weight corresponding to $(C_{10}H_{16}O_6)_{2 or 3}$ ~~2 or 3.~~ When boiled with water the ozonide decomposed and yielded H_2O_2, a ketoaldehyde or dialdehyde, and an acid which appeared to be succinic acid. The next paper (Ber. 38,1195) gave complete details of the experiment and the author's conclusions. The ozonide was prepared by passing ozonised air into a cold $CHCl_3$ solution of caoutchouc. The solvent was removed under reduced pressure and, on adding ethyl acetate followed by light petroleum, the ozonide separated as an oil which solidified on standing. Water was added and the product was distilled on steam. Levulinic aldehyde passed over and levulinic acid remained behind. If steam was only passed for a short time, levulinic aldehyde peroxide crystallised out in leaflets.

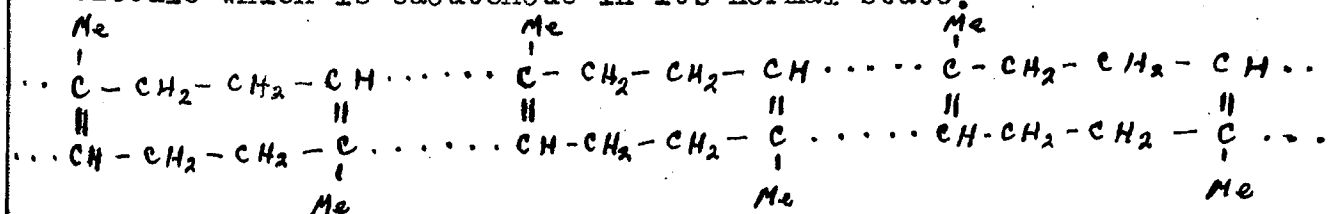
No/

No other volatile aldehyde or ketones result, and the products may be quantitatively estimated." In his first paper Harries assigned an open chain formula to rubber, but that was before he had discovered that both hydrolysis products were oxygenated at both ends, a result unobtainable from an open chain diozonide however long.

Harries assigned to caoutchouc the structure of a 1:5 dimethyl cycloocta 1:5-diene, the rupture taking place in this fashion:-



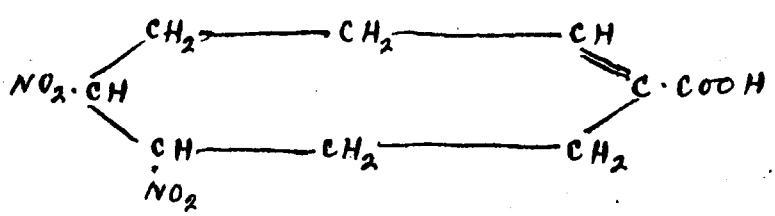
To explain the highly associated character of caoutchouc Harries made use of Thiele's theory of partial unsatisfied valencies which are always present in unsaturated compounds. Through the action of these partial valencies, an indefinite number of the cyclooctadiene rings united to form a loose molecule which is caoutchouc in its normal state.



In the presence of an oxidising agent this large loose molecule is first broken into its stable constituents, which then react to give comparatively simple products. Furthermore cis-trans isomerism is possible in a combination of this type, giving rise to a large number of isomeric bodies, which would account for the varying physical properties of caoutchoucs from different sources.

This paper resulted in a number of workers devoting their energies to preparing and decomposing ozonides of caoutchouc, whilst others proceeded to explain previous results by means of the dimethylcyclooctadiene formula. Harries himself prepared the diozonide of gutta-percha and obtained levulinic acid and aldehyde in the reverse proportions to those obtained from rubber (Ber.1905.39,85). He suggested that the gutta diozonide was a stereoisomer of the caoutchouc product.

Some time later, Alexander (Ber.1907,40,1070) returned to the nitrosite, which he prepared and analysed. His results gave a compound $C_9H_{12}O_6N_2$. To this he assigned the structure of a 5:6 dinitrocyclooctene: 1 carboxylic acid,



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This could be obtained from demethylcyclooctadiene by loss of CO_2 from the carbon holding both the nitro and the carboxyl group.

An oxidation of a different type had meanwhile been carried out by Herbert (Ber.39.1906,523), who passed air for 140 hours through a boiling benzene solution of rubber. On distilling off the solvent, he obtained a syrup from which two products were isolated. One was a red-brown syrup easily soluble in light petroleum and having the composition $C_{10}H_{16}O$. The other was a yellow amorphous friable solid, which was quite insoluble in light petroleum, and sparingly soluble in a mixture of benzene and petroleum. It had the composition $C_{10}H_{16}O_3$ and comprised only a small proportion of the yield. The author did not attempt to investigate the nature of these oxy-bodies.

Objections to Harries' 8 carbon ring formula were being raised by certain workers, notably Pickles, who shortly afterwards contributed an important paper on the subject. Meanwhile work was chiefly confined to the industrial side, especially to the preparation and vulcanisation of synthetic rubbers.

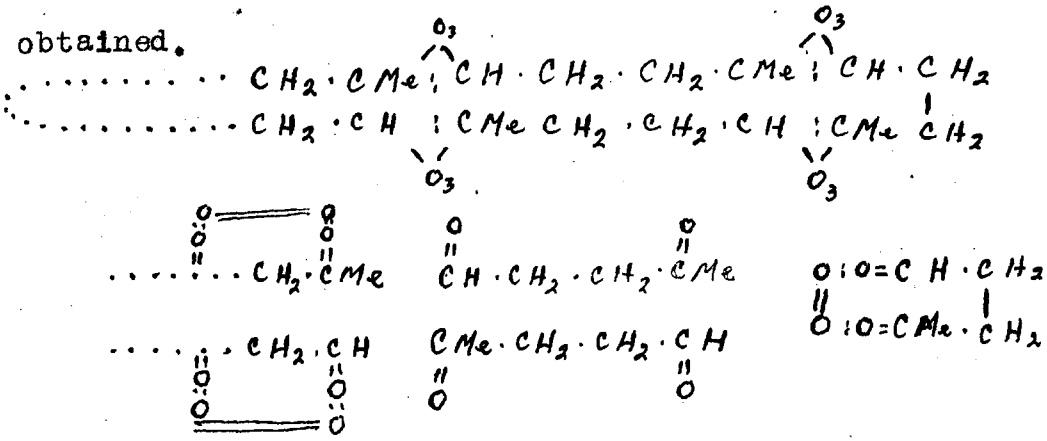
In 1911 (Ann.383,157) Harries produced "normal" and "sodium" caoutchoucs from isoprene, $\Delta^{\alpha\gamma}$ butadiene, and B γ dimethyl $\Delta^{\alpha\gamma}$ Butadiene. The normal caoutchoucs were produced by polymerisation by heat or in the presence of glacial acetic acid. The "sodium" caoutchoucs were produced/

produced by sealing the hydrocarbon in a tube along with Na wire and heating. These methods resulted in a quick and certain yield under known conditions and placed synthetic rubber on a firm foundation. The tetrabromides, nitrosites and ozonides of these caoutchoucs were prepared. The decomposition curves of the ozonides were plotted and differences were observed between the normal and sodium caoutchoucs. This decomposition curve of the ozonide was subsequently used by Harries, along with the tetrabromide, nitrosite and certain physical properties, in his definition of a "true caoutchouc". Pickles entered the field in 1910 (J.C.S.97,1.1085) with an exhaustive criticism of the dimethylcyclooctadiene formula, which he rejected for the following reasons. The 8 carbon ring formula requires two conceptions, firstly, a chemical molecule of 8 carbons, and secondly a physical (not a true chemical) polymer of unknown size. This polymer takes the form of a chemical union so loose as to allow the O_3 to depolymerise the aggregate before attaching itself to the molecules. With bromine, therefore, one of two things should happen; either the large molecule should depolymerise and furnish <u>simple</u> derivatives of formula $C_{10}H_{16}Br_4$, or it should remain polymerised and give a complex substance containing 2 Br for each $C_{10}H_{16}$ group. What the action really yields is an insoluble amorphous body of composition $(C_{10}H_{16}Br_4)_x$ which is quite as complex as caoutchouc/

caoutchouc itself. The tetrabromide is not a simple derivative of an 8 carbon ring, yet it shows the unsaturation to be expected in a simple derivative. The 8 carbon ring, therefore, involves the idea of polymerisation without diminution of unsaturation, and this polymerisation cannot be of a "loose" type if it resists the action of bromine. Other derivatives, such as the nitrosites, and hydrochlorides are equally complex and yet exhibit the high unsaturation of the 8 carbon ring.

Furthermore, complete reduction of caoutchouc should yield saturated $C_{10}H_{20}$, dimethylcyclooctane, which would be a simple compound boiling at about 170° - 180° and incapable of polymerising, yet Berthelot (Bull.Soc.Chem.1869,11.33), on reducing caoutchouc with HI and distilling, obtained hydrocarbons boiling above 350° and obviously of high molecular weight. (The hydrogenation of caoutchouc and the examination of the products of distillation had not yet been attempted, but, when tried, it yielded high boiling hydrocarbons similar to those of Berthelot.) On these grounds, Pickles contended, the dimethylcyclooctadiene structure must be rejected, and he then pointed out that the decomposition products of the ozonide could equally well be obtained from an indefinitely large single ring composed of - $CH_2.CMe{:}CH.CH_2$- nuclei. This large ring, with its double bonds evenly spaced would form an ozonide which on decomposition would give/

give levulinic aldehyde and its peroxide in the quantities obtained.



This formula permitted also of tetrabromides, nitrosites, etc. of any complexity with the required unsaturation of 2 double bonds per $C_{10}H_{16}$ group.

No further data for or against these formulae was immediately forthcoming, but researches along other lines were proceeding. In 1911 Spence and Galletley (J.A.C.S.33.190) subjected caoutchouc to a reaction which had proved very useful with terpene hydrocarbons. On acting on a CS_2 solution of caoutchouc with chromylchloride in the same solvent, they obtained a black amorphous compound $C_{10}H_{16}.2CrO_2Cl_2$ closely resembling that obtained with the terpenes. On decomposing the terpene compound with water volatile aldehydes and ketones are obtained, but this body gave a brown gummy mass. A small quantity of a substance was isolated which gave aldehyde reactions and formed a phenylhydrazone melting at 92^0.

Further/

Further investigations were promised but did not materialise.

Another oxidation was carried out by Peachey (J.S.C.I,1912,31.1103 who oxidised thin films of caoutchouc deposited in a flask, and estimated the amount of oxygen absorbed. He found this to be 4 atoms for each $C_{10}H_{16}$ group. Later, (Chem.Trade J. 1917,61,504) he repeated the experiment using dry and moist oxygen. Absorption was the same as before, and the residual gases showed the presence of CO_2 equivalent to the oxidation of 1 carbon in each $C_{40}H_{64}$. The products of oxidation were extracted with alcohol periodically and 4 substances were obtained: (1) A yellow viscid resin, neutral, and soluble in the usual organic reagents, composition $C_{16}H_{23}O_3$.

(2) a fawn coloured amorphous solid insol. petroleum, but soluble in most other organic solvents, composition $C_6H_9O_2$.

(3) Brown amorphous body soluble only in dilute alkalies, composition $C_{11}H_{16}O_4$.

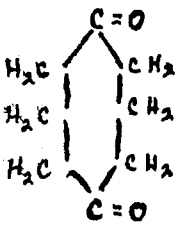
(4) Reddish-brown amorphous body, insol. alkalies, composition $C_6H_9O_2$.

No further examination was made of these substances, nor was the work correlated with similar previous experiments.

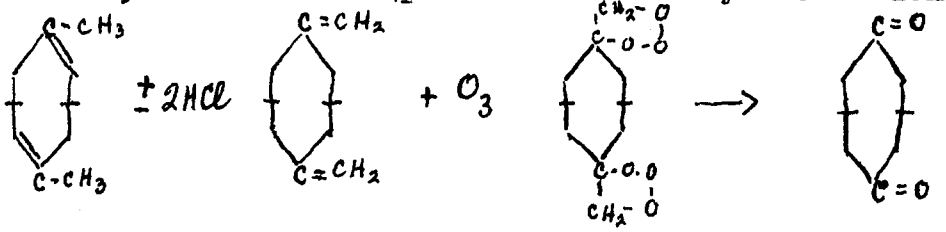
A Russian chemist Ostromisslenski was at this time investigating the polymerisation of vinyl bromide, CH_2:CH Br.(J.Russ. Phys.Chem.Soc. 1912, 44.204). The polymerised product he called "caouprene bromide" amd it resembles the bromide of butadiene synthetic caoutchouc. Caouprene bromide was compared with the tetrabromide of cyclooctadiene (Willstätter. Ber.38,1975) and/

and found to be quite different. Ostromisslenski considered that the polymerised vinylbromide must contain at least 12 carbon atoms and from its resemblance to synthetic butadiene caoutchouc, considered that the latter, and therefore natural caoutchouc could not have the 8 carbon ring structure. He advanced the same formula as Pickles, a large single ring of conjoined isoprene nuclei. A paper by Harries in 1913 (Ann. 395,211) compared the decomposition curves of the diozonides of "normal" butadiene caoutchouc and of 1:5 cyclooctadiene, a hydrocarbon prepared by Willstätter (loc.cit.) from the decomposition products of an alkaloid pseudo-pelletierin. Cyclooctadiene is a colourless oil which rapidly polymerises to form crystalline di-cyclooctadiene. According to Harries' views, butadiene caoutchouc should be a polymer of cycloocta 1:5 diene. The diozinides of both these substances were prepared and decomposed. It was found that decomposition occurred at the same rate and practically identical amounts of the decomposition product (in this case succin-dialdehyde and its acid) were obtained. Harries reaffirmed "with considerable confidence" his belief that normal caoutchouc consists of an octet ring. Continuing his study of the ozonides, Harries turned his attention to "regenerated caoutchouc" with far-reaching results.

A short paper on this subject appeared in 1913 (Ber.46,733). Additive compounds were formed with HCl, HBr, and HI, 2 mols of the acid being added to each $C_{10}H_{16}$, though it was found that synthetic Na isoprene caoutchouc during purification lost one mol./

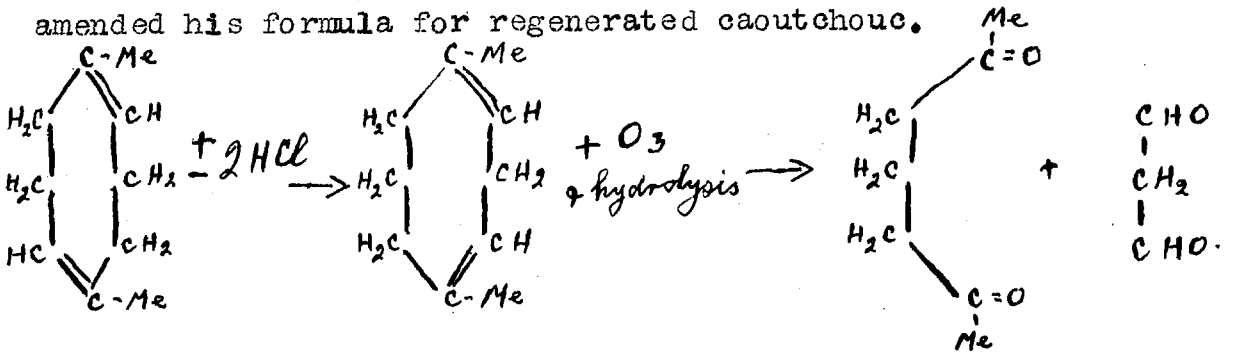
mol.of HI. The caoutchouc was regenerated by heating with sodamide or pyridine and the product so obtained resembled synthet: Na caoutchouc. The author concluded that addition and removal of the halogen acid resulted in a shifting of the ethylene leakages, in the regenerated product. He attempted to settle this point by decomposing the regenerate ozonide, and a preliminary account was published shortly afterwards (Ber.46,2590). The neutral products of the decomposition consisted of levulinic aldehyde and a ketone which Harries thought to be cyclooctane 1:5 dione  whilst

from the Ca salts formed when neutralising the original mixture, he obtained an oily keto-acid, $CH_3CO.CH_2CH_2.CH_2.CHMe.COOH$ The following structure for regenerated caoutchouc was put forward, based on the presence of the cyclooctadione.



This was amended very shortly afterwards (Ber.1914,47.784). The product which Harries had assumed to be cyclooctadione was identified as diacetyl propane, a keptanedione, $CH_3CO(CH_2)_3COCH_3$, which readily condenses with loss of water to form a methyl cyclo- hexenone. To explain the presence of this product, Harries amended/

amended his formula for regenerated caoutchouc.



This scheme required the presence of malonic dialdehyde amongst the neutral products. Harries failed to detect this and did not examine the Ca salts for malonic acid.

A thorough investigation was then carried out on a large scale and the results were given in a notable paper in 1914 (Ber.406,173). Regenerated caoutchouc was ozonised in lots of 40g. The product was decomposed with water, neutralised with $CaCO_3$ and from the neutral liquid there was obtained:-

levulinic aldehyde	9%
(levulinic acid from aldehyde)	
diacetyl propane	8.7%
(methylcyclohexenone)	
undecatrione $C_{11}H_{18}O_3$	.9%
pentadecatetrone $C_{15}H_{24}O_4$	.06%

Unidentified fractions and ketone residues.

The Ca salts on acidification gave:-

HCOOH -	18.3%
$(COOH)_2$	trace
levulinic acid	12%
Succinic "	1.5%
Hydrochelidonic	1.7% — HOOC·H₂C·H₂C·CO·CH₂·CH₂·COOH
Methylcyclohexenone-acetic acid	1.7%
unidentified acids and resin.	

It was obvious that these products could not be harmonised with a ring structure containing only 8 carbons. It indicated rather, that a very large single ring, with double bonds unsymmetrically placed, had been ruptured at these bonds, and the above products were simply long and short fragments of the chain, oxygenated at both ends. The appearance of the ketone $C_{15}H_{24}O_4$ seemed to indicate at least a 20 carbon ring, $C_{25}H_{40}$. The molecular weight of this ozonide in benzene gave a value 535, whilst $C_{25}H_{40}O_{15}$ requires 580, though Harries did not place much reliance on this. Some of the regenerated caoutchouc was again treated with HCl followed by pyridine, giving "Regenerate II". This, when ozonised and decomposed gave a much larger proportion of high boiling constituents, indicating a further re-arrangement of the ethenoid linkages of Regenerate I.

In the face of this definite evidence, Harries now withdrew the cyclooctadiene structure and adopted the structure already proposed by Pickles, a large single ring consisting of 8 or more - $CH_2.CMe{:}CH.CH_2$ - nuclei. Such a structure satisfied the following requirements: (1) it showed a high molecular weight. (2) it would be unsaturated to the extent of 1 double bond in each C_5H_8 nucleus (3) provided the double bonds were symmetrically placed, on rupture, it would yield only derivatives of levalinic aldehyde (4) if any extensive rearrangement in the double linkages occurred, straight chain compounds/

compounds of greatly varying lengths would be obtained when the compound was ruptured at these linkages. The thermal dissociation of the hydrochloride supplied some confirmation of the size of the molecule. Heated in vacuo at 100°, HCl was lost till the Cl content corresponded to that of a body $C_{30}H_{48}$. 6HCl which had lost all but 1 molecule of HCl.

This paper was so conclusive that it discouraged the usual host of imitators, and research was diverted into other channels. Ostromisslenski (J.Russ.Phys.Chem.Soc.47,1910) recorded further investigations into caouprene bromide which he declared to be isomeric with the bromide of synthetic erythrene caoutchouc. Both, on removal of HBr gave dehydrocaouprene, $C_{32}H_{32}$ the corresponding body obtained from the bromide of natural caoutchouc being the homologue $C_{32}H_{24}Me_8$. The molecular weight of caouprene bromide in ethylene bromide was in agreement with the formula. An interesting speculation as to the formation of rubber in the plant was included. Isoprene heated cautiously to 80-90° gives a hydrocarbon $C_{10}H_{16}$ with 3 double bonds, two being conjugated. To this hydrocarbon, B Myrcene, he assigns the structure CH_2:CH.CMe:CH.CH_2.CH_2.CMe: CH_2.

Heated with BaO_2 and Na this is converted quantitatively into normal isoprene caoutchouc. It is suggested that the formation of the latex in the plant is via B Myrcene, formed by the dehydration of such alcohols as geraniol, linalool and nerol, all of which have a B.Myrcene structure.

An/

An interesting oxidation was carried out by Kirchhof (Koll.Zeitsch. 27, 311 and 30.176). This author, who had previously obtained amorphous bodies of composition $C_{10}H_{16}O$ and $C_{10}H_{16}O_3$ by the oxidation of caoutchouc in air at 100° (Koll.Zeit.13.49), succeeded in effecting a controlled oxidation by means of H_2SO_4. A CCl_4 solution of caoutchouc treated with conc.H_2SO_4 yielded first a hydrocarbon which had none of the physical properties of rubber. Its composition, on analysis, seemed to be $C_{10}H_{15}$. [This author contended that Para had the composition $(C_{10}H_{17})_X$: whilst African Congo was $(C_{10}H_{16})_X$]. This hydrocarbon with Br_2 and S gave products $C_{20}H_{30}Br_2$ and $C_{20}H_{30}S$, suggesting a rearrangement of the double linkages to give bridge formation and tetramethylene rings.

The prolonged action of H_2SO_4 on a cold C_6H_6 solution of caoutchouc yielded a red, acetone-soluble product with an intense aromatic odour, soluble in alcoholic KOH, from which it was reprecipitated by acids, and also reducing Fehling's solution. It had the composition $C_{20}H_{30}O_3$, and formed a crystalline phenylhydrazone, MP 120-124°. Kirchhof suggested that this was a spiral chain, with - CHO and -COOH groups at its ends.

Examination of the completely hydrogenated product of caoutchouc was a task which had been rendered necessary in the light of Pickles' criticisms. This had previously been carried out by Berthelot in 1869 using HI, and was now repeated by/

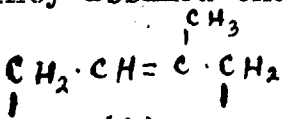
by Staudinger and Fritschi (Helv.Chim.Acta.1922,5.785) using hydrogen at 270° 4100 atmos. in presence of a catalyst. The product had the pomposition $(C_5H_{10})_x$, and was completely colloidal like caoutchouc, suggesting a large ring or a very high paraffin where $C_nH_{2n} = C_nH_{2n+2}$; it was also stable to Br_2 except on long standing in sunlight. It was therefore a compound of high molecular weight and upheld Pickles' contention that complete saturation, and therefore destruction of double bonds and partial valencies, would not yield a simple, low-boiling, $C_{10}H_{20}$ hydrocarbon. Comparative distillations of this body and caoutchouc under reduced pressure gave the following results:-

Caoutchouc.	Hydrogenated Product.
Decomp.Temp.(1 - .3mm) 275-320°	350 - 390°
Products:- isoprene, dipentene $C_{15}H_{24}$; $C_{20}H_{32}$; $C_{25}H_{40}$.	All products $(C_5H_{10})_x$ with only 1 double bond. Lowest C_5H_{10}, BP 30-40°. βmethyl α butylene. Highest $C_{50}H_{100}$.

This seems to show conclusively that no depolymerisation into simpler molecules occurs on saturation.

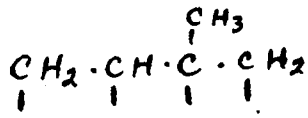
Plummerer and Bankard (Ber.55 - 3458) hydrogenated caoutchouc in very dilute solution at 70° and atmospheric pressure, using Pt. sponge as catalyst. The product was an elastic body, saturated to Br_2 and having the composition $(C_5H_{10})_x$. In solution, this substance rapidly absorbed a volume of oxygen equal to half the volume of hydrogen originally/

originally absorbed. The resulting product which seemed to be a hydrocarbon dissolved easily and rapidly in ether without any swelling. In solution it again absorbed as much hydrogen as the original caoutchouc. This work was confirmed by Harries (Ber.1923,1048) who added details of the experimental conditions. A novel method of attacking the problem was used by Boswell and his workers (Trans.Roy.Soc. Canada 1922, 16,III.27). They assumed that isoprene polymerises in two fashions, either



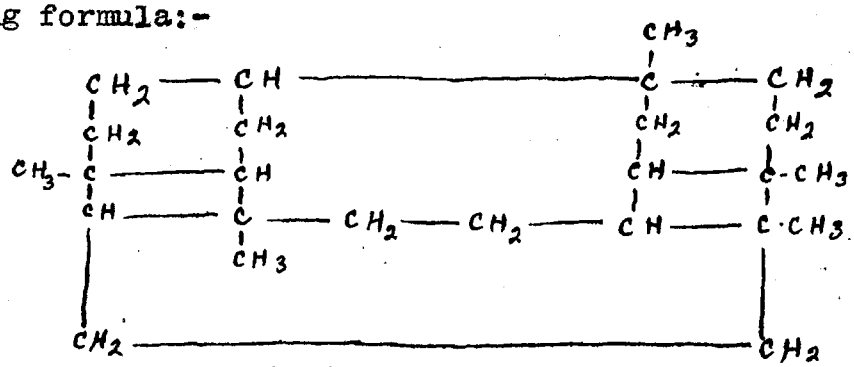
(a)

or



(b)

They constructed a formula by uniting 1 molecule (b) with 2 molecules (a), and the resulting structure, which contained 2 ethylene linkages, was completed by the addition of 2 more molecules (b). This gave a hydrocarbon $C_{25}H_{40}$ of the following formula:-



This structure could yield any required product from C_5H_8 to $C_{25}H_{40}$ including dipentene and dimethylcyclo-octadiene, and the latter, of course, would yield a diozonide giving the usual decomposition products, but the yield would not be quantitative. This, the authors claim, is in accordance with fact./

fact. To test this formula, oxidations were carried out by various means and the products were analysed. It was then shown that the various products of each oxidation could be fitted together so as to yield a parent structure such as that postulated.

The oxidations were conducted with $C Cl_4$ solutions, which were shaken with aqueous $KMnO_4$, and with dilute H_2O_2, also a thin sheet was oxidised by exposure to the air. By precipitation from solvents, bodies were isolated which varied in composition from $C_{30}H_{48}O$ to $C_{25}H_{40}O_9$, while a compound $C_{25}H_{40}O_8I$ was obtained by the use of H_2O_2 and iodine. Formulae were assigned to all these compounds on the basis of the above structure or fragments thereof. This formula, however, completely fails to explain the unsaturated character of rubber as exhibited by the various addition compounds of high molecular weight.

OBJECT AND RESULTS OF PRESENT WORK.

The conclusion to be drawn from the mass of investigation just reviewed is that the caoutchouc molecule consists of a number of - $CH_2.CMe.CH.CH_2$ - nuclei united to form a large single ring, the double bonds being arranged in a symmetrical fashion. The cyclooctadiene formula must be rejected: it was introduced to explain one reaction only and has failed to be of any further use. It is now fully recognised that the caoutchouc molecule is an exceptionally large one, and to co-ordinate this with an eight carbon ring requires a conception of polymerisation without decrease in unsaturation which is wholly foreign to our present knowledge of chemical combination. Claims to have depolymarised caoutchouc into simpler molecules do not stand examination. Schmitz (Gummi. Ztg. 34-167) claims to have accomplished this by boiling for 10 hrs. in xylene at 130-160° and 15 atmos., but the bromide of this product seems to be of the same order of complexity as that obtained by more usual methods. In considering these claims it must be remembered that different physical modifications of caoutchouc were described by Harries (Ann.383. 157) one of which, the (c) or oily form gave less viscous solutions than the ordinary form. Yet this substance was a colloid and yielded the same tetrabromide and nitrosite as the normal form. This (c) form is probably the explanation of all depolymerisation claims, especially as it is formed by the method usually adopted to depolymerise, i.e. by prolonged heating of a caoutchouc/

caoutchouc solution.

The large ring formula does not suffer from these disadvantages. It furnishes an equally good explanation of the ozonide and its products; it successfully depicts the unsaturated nature of caoutchouc; no idea of polymerisation or depolymerisation is involved, and it permits of complete saturation of the molecule without disruption.

Accepting this formula, it remains to be ascertained how many isoprene nuclei go to form this large ring. Molecular weight determinations by the usual methods fail because of the colloidal nature of the material, and the extreme difficulty of freeing it from impurities. Caouprene bromide, prepared by Ostromisslenski, is of the same order as caoutchouc, and its ~~molelucar~~ molecular weight in ethylene bromide points to it containing a 32 carbon ring. Harries and Evers (Wiss. Veröffentl, Siemens, Konz. 1.87), by reducing caoutchouc hydrochloride with Zn dust obtained a hydrocarbon whose molecular weight in bromoform agreed with $C_{35}H_{62}$ or $C_{40}H_{70}$. To the derivatives of rubber obtained by various oxidation methods and characterised by ultimate analysis, objection is taken on the grounds that in few cases was it certain that an individual compound had been obtained, that considerable degradation of the caoutchouc molecule was possible during the oxidation, and that the results of ultimate analysis of a complex body containing carbon, hydrogen, and oxygen are not sufficiently accurate to characterise the body. For instance/

instance, products of the order $C_{10}H_{16}O_3$ so often obtained from caoutchouc might be equally well described from the results of their analyses as $C_{25}H_{40}O_8$ or $C_{30}H_{48}O_{10}$. On the other hand the analysis of a characteristic derivative such as the nitrobenzoate of an alcohol or the phenylhydrazone of an aldehyde might prove of great value, but few investigators seem to have made any inquiry into the nature of their products with a view to obtaining such derivatives.

Kirchhof's aldehyde-acid, which yielded a phenylhydrazone, is the type of compound which may ultimately fix the size of the caoutchouc molecule, though in this particular case it is probable that degradation of the caoutchouc molecule occurred to a great extent during the prolonged treatment with H_2SO_4, no special precautions having been taken to avoid this.

The present work was started, therefore, with two objects in view, firstly, to oxidise caoutchouc by some mild process which would ensure the molecule being preserved in its entirety, and secondly to examine the product for some characteristic grouping whereby a pure derivative might be prepared. By analysis of this derivative it was hoped to obtain some idea of the size of the hydrocarbon molecule.

The method of oxidation chosen was that which has proved so successful in the hands of Henderson and his workers, (Trans.Chem.Soc. 99-1539, 101,2288, 103, 1543 etc.) in the investigation of the alkaloids and terpenes, namely, the use/

use of 100 vol. H_2O_2 in glacial acetic acid. This reaction usually results in the production of hydroxy-bodies by the addition of -OH at the double bonds of unsaturated compounds, though in a few cases ketones are formed, also inner oxides, by the elimination of water between two hydroxyls, adjacent, or in the 1:4 position. The method has the advantage of being easily controlled, and, by suitable regulation of the temperature, the formation of resins can be avoided to a large extent. The main product of the reaction almost invariably retains intact the original hydrocarbon structure.

Considerable modifications of the process were, of course, entailed, owing to the colloidal nature of caoutchouc and to the fact that it is insoluble in glacial acetic acid, but these difficulties were overcome and a good yield of the oxidation product was obtained, the formation of tarry matter being successfully avoided. The oxidation product, in the form of an odourless amorphous white powder, exhibited properties very similar to those of the terpene products obtained by the same process. It was insoluble in water and light petroleum, very sparingly soluble in ether, and easily soluble in benzene, alcohol, (ethyl and methyl), glacial acetic acid, chloroform and pyridine. Analysis gave figures which approximated to some multiple of $C_{10}H_{18}O_3$ and the molecular weight in benzene by the cryoscopic method exceeded 1000. This seemed to indicate a compound of 60 carbon atoms, but no great weight was attached/

attached to these figures, as the method of purification of the product - precipitation from C_6H_6 solution by means of light petroleum - could not be considered satisfactory.

To test the alcoholic properties of this product, suggested by its superficial resemblance to the terpene products obtained by the same process, an attempt was made to prepare a nitrobenzoyl ester, a very suitable derivative for analytical purposes. This, however, was not completely successful. Considerable resinification occurred, and the ester, which was amorphous, could only be separated from the unattacked alcohol by the greater solubility of the former in ether, in which, however, the resin was also soluble. Analysis of different batches of this product proving most unsatisfactory, the preparation was abandoned and other derivatives sought.

As all the products of this series were non-volatile and amorphous, the complete separation of resinous by-products was impossible. Any method of preparation, therefore, which could not be modified to give a derivative free from resin, was at once rejected.

Attempts to prepare the phenylurethane and the acid phthalate were also unsatisfactory. In the former case, the alcohol was recovered unchanged after the reaction, and, in the latter, the ester contained much resinous matter. Incidentally the phthalate does not lend itself to such accurate characterisation as a nitrogen compound, being more useful as

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a means of obtaining a pure specimen of the alcohol by subsequent hydrolysis.

As the alcohol seemed to yield no suitable derivative, attention was directed to the preparation of an aldehyde or ketone by oxidation.

A suitable method of preparing the aldehyde or ketone from the corresponding alcohol is by oxidation with CrO_3 in glacial acetic acid solution. If the theoretical quantity of this reagent is used, a smooth oxidation results, no acid or resinous compounds being formed. This reaction, slightly modified, yielded with the caoutchouc compound a greenish-yellow, pleasant-smelling syrup, soluble in ether, which gave aldehyde reactions with ammoniacal silver oxide, and Fehling's solution. On long exposure to the air this substance darkened in colour, and small quantities of an acid were obtained.

After numerous attempts to determine the correct quantity of CrO_3 necessary to effect the oxidation, good yields of this aldehyde were obtained, free from resin and degradation products.

On treatment in alcoholic solution with an excess of semicarbazide acetate, the aldehyde formed a semicarbazone, which was first obtained as a light brown paste by the cautious addition of water to the reaction solution. This paste retained only a faint trace of the aldehyde odour, and was practically free from resin.

This/

This result was so encouraging that it was considered that the object of the investigation would be ~~obtained~~ attained if this derivative were submitted to an exhaustive purification and analysed. Methods of purification were therefore studied. As attempts to crystallise the compound were not successful, the method adopted was the systematic removal of each of the constituents and possible by-products of the reaction by which the semicarbazone was formed. Considerable loss occurred, as any doubtful portion was immediately rejected, before the product was finally obtained in the form of a white amorphous powder. This powder was insoluble in water, ether, and benzene, and extremely soluble in alcohol, acetone and ethyl acetate. It was quite odourless and on long exposure to the air showed no tendency to acquire a pink tinge, indicating the absence of free aldehyde. Analysis of different batches yielded closely agreeing results.

The conclusions formed as the result of this work are based entirely on the composition of this semicarbazone and its production from the caoutchouc hydrocarbon, and before considering these conclusions, the links in the chain may profitably be re-examined. The alcohol was produced from caoutchouc by a method which can be relied upon not to rupture the hydrocarbon molecule. Judging by the yield and the fact that no other products could be detected in the reaction solution, this alcohol is the sole product of the oxidation. It is of high molecular weight and colloidal, and on distillation in vacuo it decomposes

to/

to give a dark oil very similar to that obtained from caoutchouc itself. When burned it emits the characteristic odour of burned caoutchouc. This alcohol, therefore, would appear to retain, almost complete, the skeleton of the caoutchouc hydrocarbon. A small amount of CO_2 is evolved during the early stages of the oxidation; this occurred during every oxidation and seems to be an integral part of the reaction. As will be seen under "Experimental" this CO_2 was difficult to measure, but seemed to approximate to the oxidation of one out of 40-45 carbon atoms.

The production of the aldehyde from the alcohol was also accomplished by a method which usually yields the direct derivative if the theoretical quantity of CrO_3 is used. By-products of a resinous and acid character were certainly obtained during this oxidation, and the yield was not theoretical, but this was due to a large extent to the fact that the alcohol is very easily oxidised, and, on addition of the CrO_3 solution, even to a well cooled solution of the alcohol, a certain amount of local oxidation occurred before the solutions were properly mixed. The aldehyde, however, was also non-volatile in steam and decomposed on distillation under reduced pressure; it emitted the characteristic odour when burned, and its semicarbazone was amorphous. It may therefore be said with considerable confidence that this aldehyde is a direct derivative, and not an oxidised fragment, of the original caoutchouc molecule.

In the preparation of the semicarbazone, sufficient semicarbazide acetate was used to react with all the oxygen atoms

if/

if necessary, and in the purification of the product all the possible impurities, i.e. unchanged aldehyde and non-aldehyde compounds, KCl, semicarbazide, acetate, and condensation products of semicarbazide, were dealt with and eliminated in turn.

The analysis of the semicarbazone therefore should give reliable data as to the size of the original hydro-carbon molecule.

The mean nitrogen content (see "Experimental") was found to be 7.1%. Assuming the derivative to be a mono-semicarbazone, this 7.1% represents the weight of 3 nitrogen atoms, which places the ~~molecular~~ molecular weight of the body in the region of 590. The percentages of C and H were 60.1 and 8.8 respectively, figures which correspond closely to the semicarbazone of an aldehyde $C_{29}H_{50}O_9$ or $C_{28}H_{49}O_8 . CHO$. The figures obtained from the analysis of the alcohol may now be interpreted. These agreed roughly with an empirical formula $C_{10}H_{18}O_3$, the oxygen content being rather short of this figure. On a basis of C_{29}, these figures show the composition of the alcohol to be $C_{29}H_{52}O_8$ or $C_{28}H_{49}O_7 . CH_2OH$, whereas the alcohol corresponding to the above aldehyde should have the composition $C_{28}.H_{49}O_8.CH_2OH$. The explanation of this discrepancy must be looked for either in the purity of the alcohol or in the process of oxidation to aldehyde. Absolute purity is not claimed for the alcohol, as in its preparation no special endeavour was made to eliminate the traces of ~~by-products~~ foreign bodies - especially of a protein nature - which/

which would undoubtedly be present. To test the second alternative, comparative oxidations were carried out using the theoretical quantities of CrO_3 necessary to effect the changes (a) $C_{29}H_{52}O_9 + O = C_{29}H_{50}O_9 + H_2O$ and

(b) $C_{29}H_{52}O_8 + 2O = C_{29}H_{50}O_9 + H_2O$.

In (a) the yield of aldehyde was good, the product being almost colourless, whilst in the case of (b) a much smaller yield of dark coloured aldehyde was obtained, along with a quantity of gelatinous matter containing chromium, apparently the chromium salt of a resinous acid.

From these results it may safely be assumed that it is the purity of the alcohol which is at fault, and not the process of oxidation to aldehyde. The correct figures therefore are, for the aldehyde, $C_{29}H_{50}O_9$, and for the alcohol $C_{29}H_{52}O_9$. If the semicarbazone is that of a mono-aldehyde containing 29 carbon atoms, then the parent hydrocarbon cannot have less than 30 of such atoms grouped in a 24 carbon ring, the oxidation of one of the methyl side chains accounting for the CO_2 evolved during the early stages of the oxidation.

The simplest structure which can be assigned to rubber is therefore 6 - $CH_2.CH{:}CMe.CH_2$ - nuclei united to form a large single ring.

The analysis, of course, does not preclude the possibility of the aldehyde being a dialdehyde of 58 carbons which forms

a/

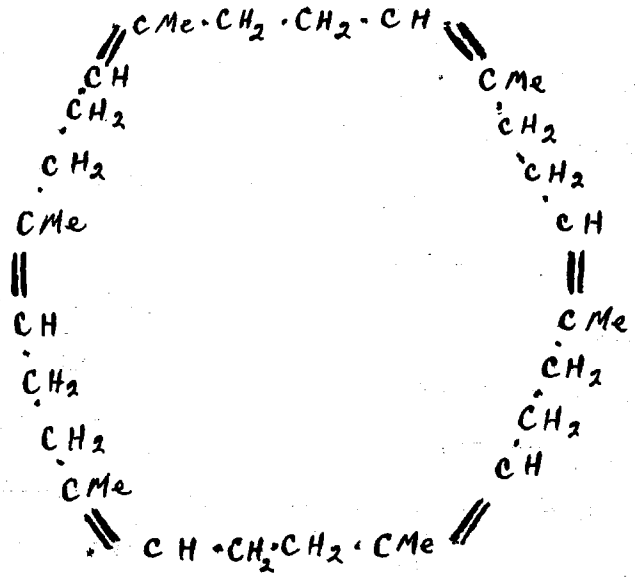
a di-semicarbazone; indeed, the molecular weight of the alcohol in benzene would seem to bear this out, since $C_{29}H_{52}O_9$ = 544 whilst the determination actually yielded the figures 991, 1053 and 997. No great reliance can be placed on this, however, since, on the one hand, association of the solute may occur in benzene solution, and on the other, the solution was undoubtedly of a colloidal nature.

An attempt was made to settle this point by a chemical method, namely, that of obtaining the corresponding acid from the aldehyde, followed by the preparation and analysis of a salt. The result, however, was inconclusive. Oxidation of the aldehyde by means of very dilute HNO_3 resulted in a body which had no acidic properties whatever. A method of gentle spontaneous oxidation was then tried which yielded a certain proportion of a resinous acid.

The insoluble lead salt of this acid was obtained, and on analysis was found to contain 26.43% Pb. The molecular weight of the salt is therefore 784, and if the salt is normal the acid must be a dibasic acid of molelucar weight 784-207 + 2 = 579. This is not the normal oxidation product of a mono-aldehyde of molecular weight 542. On the other hand, the figures agree closely if the lead salt is of the type $Pb\begin{matrix}OH\\R\end{matrix}$, a basic salt sometimes obtained from weak acids. This is supported by the fact that the silver salt decomposed almost completely while being washed. There is, therefore, not sufficient evidence to differentiate with confidence between a mono-aldehyde/

mono-aldehyde of 29 carbons, and a di-aldehyde of 58 carbons.

Previous research has settled beyond question that the caoutchouc molecule consists of an unknown number of isoprene nuclei united to form a large single ring. In the present investigation the hydrocarbon has yielded a derivative obtainable only from a structure of 30 carbon atoms or a multiple thereof. The simplest structure therefore, which can be assigned to caoutchouc, is the following:-



Experimental.

Purification of Material and Preliminary Experiments.

The caoutchouc used was Plantation Pale Crepe, which had been washed and rolled, and was in the form of thin sheets, almost white, and free from the usual resinous odour. This was cut into thin strips and purified by extraction with acetone in a Soxhlet apparatus for 10 hours. Owing to the nature of the material, complete removal of the resin is not possible by simple acetone extraction, but the more thorough method of dissolving in benzene, filtering and precipitating the caoutchouc by the addition of alcohol was not considered necessary in view of the purification which the oxidation product would undergo; and the fact that analysis of the first oxidation product was not the object of the work. The caoutchouc, after extraction, was nearly transparent and colourless, and had to be preserved out of contact with the air, as it oxidised rapidly.

The method of oxidation elaborated by Henderson (loc.cit.) consists in dissolving 50 gs. of the terpene hydrocarbon in 300 g. glacial acetic acid and adding the calculated quantity of H_2O_2 (100 vol.) equivalent to 2 mols. H_2O_2 to each $C_{10}H_{16}$ molecule. A proportion of the hydrocarbon separates and forms a layer on the surface, but this gradually dissolves as oxidation of the terpene in solution proceeds. The reaction is promoted by maintaining the mixture at a temperature of about 50°C.

By/

y control of th· temperature, resinous products, as evidenced by he darkening of the solution, can be avoided to a large extent, hile the reaction can, of course, be stopped at any stage and the products examined. Completion of the reaction is indicated when he remnant of the surface layer shows no further tendency to dissolve, nd the products are then obtained by neutralisation of the acid and extraction with ether.

The mechanism of the reaction is not clear, but it seems that oxidation occurs through the formation and decomposition of peracetic acid. It has been found that with inert solvents such as CCl_4, oxidation frequently does not take place.

As it was intended to adhere as closely as possible to these reaction conditions, the behaviour of caoutchouc towards glacial acetic acid was studied. Finely cut caoutchouc in acetic acid was allowed to stand in stoppered flasks. Considerable swelling occurred during the first three days, but even at the end of a month the separate pieces retained their identity, and the acid could be obtained ~~y~~ pure by filtration. Heating merely accelerated the swelling.

Attention was then directed to mixing acetic acid with a solution of caoutchouc in one of the usual solvents. It was found that on small quantities of the acid being added to a $CHCl_3$ solution of caoutchouc, the initial precipitate redissolved on shaking and the resulting solution had a considerably decreased viscosity. Further quantities of acid were added till a point was reached where the precipitate of caoutchouc failed to redissolve. A small quantity of water, representing H_2O ?

solution/

solution, was then added. This precipitated more caoutchouc which redissolved to a certain extent on vigorous shaking. The mixture then consisted of a layer of clotted caoutchouc over a solution which was almost colourless and of very low viscosity. That this solution contained a considerable proportion of the caoutchouc was proved by withdrawing a quantity and precipitating the caoutchouc with water.

It was therefore evident that a solution could be prepared analogous to that required in the terpene oxidation: it remained to be discovered whether the bulk of this solution could be maintained at a reasonable figure, and yet permit of the oxidation of a fair quantity of caoutchouc. Twenty-five grams of caoutchouc was dissolved in 850 cc. $CHCl_3$. Two days were required for complete solution, and it was noted that while boiling had no effect on the rate of solution, vigorous agitation accelerated it. The solution obtained was opaque, of a brownish colour and extremely viscous. Glacial acetic acid was then added in quantities of 30-40 c.c. with vigorous shaking. On each addition a quantity of caoutchouc was precipitated, but this dissolved on further agitation. After 180 c.c. acid had been added the precipitated caoutchouc became difficultly soluble, and it was then found that heating the mixture to 70-80° under reflux effected solution. By this method a total of 230 ccs. acetic acid was added, which was considered sufficient for the purpose. The solution was brown, opaque and of very low viscosity. As a surface layer of caoutchouc did not/

not form until some time after the solution had cooled, it was considered possible to reduce the $CHCl_3$ content.

Distillation was carried out on the water-bath, and when about 150 c.c. $CHCl_3$ had been collected the presence of undissolved caoutchouc was noted. This was redissolved by agitation and the distillation repeated. In all, 500 c.c. $CHCl_3$ was removed before the precipitated caoutchouc failed to redissolve in the hot solution. When cool, the liquid under the caoutchouc layer was opaque, of a brownish colour, and seemed as mobile as water.

The reaction mixture consisted of:-

25 gm. caoutchouc.

350 c.c. $CHCl_3$

230 c.c. CH_3COOH

and, in all later experiments, was prepared directly by dissolving 25 gm. caoutchouc in 350 c.c. $CHCl_3$. Solution required 2 days, and yielded an extremely viscous jelly. 200 c.c. acetic acid was then added in lots of 50 c.c. with vigorous agitation. The solution was then heated to boiling and the remaining 30 c.c. acid added. When cool, this solution was identical with that obtained by using an excess of $CHCl_3$, with subsequent removal of the excess.

In the trial oxidation, 65 gm. (3 mols.) of 30% H_2O_2 was used as against 45 gm. (2 mols) in the corresponding terpene oxidation. Addition of the perhydrol caused a further precipitation of caoutchouc.

The/

The flask was fitted with a reflux condenser and maintained at a constant temperature of 50°C in the waterbath. The first action observed was the clearing of the liquid portion of the mixture, which became colourless and transparent in the course of about 6 hours. This was followed by the slow and persistent evolution of a gas, later identified as CO_2. A change also occurred in the layer of caoutchouc which gradually became liquid. This is possibly the C modification of caoutchouc described by Harries (loc.cit.) A further 18-20 hours heating resulted in the complete disappearance of the caoutchouc layer to yield a clear colourless solution. Evolution of CO_2 also ceased shortly after this point.

The solution acquired a green tinge after a further 12 hours, this tinge changing gradually to light yellow. The development of this colour occupied several days, resulting in a clear golden-yellow solution. A sudden change then took place in the course of a few hours, the solution turning first pink, then deep red, and on further heating the colour grew deeper and the solution became opaque.

The reaction was stopped at this point as it was obvious that the oxidation had proceeded too far, and was yielding resinous products. The solution was poured into a large volume of water and well shaken. On standing, the $CHCl_3$ settled, carrying with it the dark coloured product, the aqueous layer retaining most of the acetic acid. The chloroform layer was drawn off and the aqueous layer extracted with more chloroform/

chloroform. The combined extracts were first washed with dilute Na_2CO_3, then with water, and finally dried over anhydrous Na_2SO_4. On distilling off the $CHCl_3$, the product was obtained as a dark red syrup with a pleasant fruity odour. It was soluble in alcohol, ether and acetone, and sparingly soluble in benzene. It was not volatile in steam, and decomposed at a high temperature under reduced pressure. On boiling with alcoholic KOH, and neutralising the alkali with CO_2, an ethereal extract was obtained which yielded a yellow syrup on distillation of the solvent. This was probably a remnant of the product existing at the golden-yellow stage of the oxidation. The alcoholic solution was acidified and large quantities of a resinous acid were obtained. These products were not further examined, and this concluded the preliminary work which had yielded the following information:- that an oxidation of caoutchouc was possible under conditions similar to the oxidation of the terpenes; that the oxidation took place in two stages, the first stage being the clear yellow solution, and the second stage, the opaque solution which yielded resins; that the oxidation could be controlled by reducing the amount of H_2O_2 (2 mols. per $C_{10}H_{16}$ is the quantity used in terpene oxidations) and by stopping the reaction before the red colour developed.

Subsequent experiments were suitably modified with gratifying results. As it was expected, and later verified, that true caoutchouc derivatives would be non-volatile and amorphous, the problem/

problem of resinous and tarry by-products received great consideration. Once formed, these impurities could only be removed by extraction with solvents, or precipitation from solution, neither method being really satisfactory. With this in view, all reactions entailed in the preparation of derivatives were studied, and modified more or less extensively.

The Oxidation.

A solution was prepared as previously detailed, consisting of 25 gm. acetone-extracted caoutchouc, 350 c.c. $CHCl_3$, and 230 cc. glacial CH_3COOH. To this was added 45 gm (2 mols) of 30% H_2O_2 and the mixture was maintained at a temperature of 50^0 on the water bath.

With the smaller quantity of H_2O_2, the various changes previously noted, the clearing of the liquid portion, liquefaction of the caoutchouc layer, and the gradual solution of this layer, took longer to accomplish. When a homogeneous solution had been attained, and evolution of CO_2 had ceased, the reaction was carefully watched and was stopped as soon as the yellow tinge developed.

The solution was poured into a-bout a litre of water and well shaken. The chloroform layer was separated and the aqueous portion again extracted with chloroform. Considerable emulsification took place, but with the addition of small quantities of alcohol, a separation was effected on standing overnight/

overnight.

Solid K_2CO_3 was added to the chloroform solution to remove the last of the acetic acid, and when all action had ceased, the solution was again washed with water and dried over anhydrous Na_2SO_4. The chloroform solution was clear, mobile and of a light yellow colour, and, on removal of the solvent by distillation, the product was obtained as a clear yellowish syrup.

As the reaction was stopped at a purely arbitrary point, there was a possibility of the product containing unattacked caoutchouc. This would be removed by two methods:- (a) by dissolving the syrup in a large volume of alcohol and allowing the unsoluble caoutchouc to settle. The clear solution was then decanted and the alcohol distilled off; (b) by dissolving the syrup in just sufficient benzene to yield a mobile solution, and adding a large volume of petroleum ether. The product is completely precipitated as a thick white paste, and any caoutchouc present remains in the mixed solvents. The second method is preferred, as it gives a product which is easily dried and powdered.

The water which had been used in the separation and washing of the product was filtered to remove emulsion and examined. Only acetic acid, $CHCl_3$ and traces of the syrup were found present, indicating that no water-soluble degradation products are formed by the oxidation. This oxidation has been repeated many times and has always yielded the same product. An interesting observation is that if the oxidation has been allowed/

allowed to proceed too far, resulting in the development of the pink colour, immediate cooling of the solution results in the gradual disappearance of this colour, and the product obtained is quite free from resin. Modifications of this method of oxidation have been tried but do not offer any advantage. Using CCl_4 instead of $CHCl_3$, it was found that a much larger proportion of caoutchouc remained in the surface layer, whilst the H_2O_2 was not very soluble in the CCl_4-CH_3COOH mixture and tended to layer out with the caoutchouc on the surface. The oxidation took much longer, but yielded the usual product. Oxidation in a very dilute solution (.7%) was also tried. The solution consisted of 7 gm. caoutchouc 450 cc. $CHCL_3$, 325 cc. CH_3COOH, 12.6 gm. H_2O_2. Only a thin layer of caoutchouc remained on the surface, and this soon disappeared on heating. The oxidation proceeded rapidly and constant observation was necessary to arrest the reaction before it had proceeded too far. The usual product was also obtained in this case.

The Oxidation Product.

Precipitated from benzene by an excess of petroleum ether, the product was obtained in the form of a thick white paste. This was washed with petroleum ether, dried in vacuo and powdered. The yield, from 25 gm. rubber, was 28-30 gm. of an odourless white powder, insoluble in water and petroleum, very sparingly soluble in ether, and easily soluble in alcohol/

alcohol(ethyl and methyl), acetone, benzene, chloroform, acetic acid and pyridine. It did not react with alkali carbonate solution, but on long standing with dilute NaOH, and more quickly on heating, it turned dark red and seemed to dissolve to some extent, giving a red flocculent precipitate on acidification. All attempts to crystallise it from solvents and mixtures of solvents failed. When burned, it emitted the characteristic odour of burned caoutchouc. It was non-volatile in steam, and under reduced pressure it decomposed at a high temperature and yielded water and a dark oil very similar to that obtained on distilling caoutchouc. It did not react with semicarbazide acetate, and as already stated, was unaffected by Na_2CO_3. Boiling with alcoholic KOH caused extensive resinification, the products recovered being a small amount of the original substance and, on acidification of the solution, a large quantity of resin of an acid character. Hydrolysis using reagents such as barynta, and dilute H_2SO_4 also yielded tarry products. Tests with Br_2 and alkaline $KMnO_4$ showed the product to be unsaturated. The above properties seemed to confirm the view that this product is a hydroxy-body closely related to the original hydrocarbon.

A portion, dissolved in benzene, filtered and precipitated as before, yielded the following results on analysis:-

(a) .2201 gm. gave .5368 gm. CO_2 and .1915 gm. H_2O

(b) .2042 gm. gave .4956 gm. CO_2 and .1757 gm. H_2O.

Found/

Found	C	H	O
	(a) 66.51	9.665	23.8
	(b) 66.19	9.56	24.25
$C_{29}H_{52}O_8$ requires	65.92	9.849	24.24
$C_{29}H_{50}O_8$ requires	66.16	9.506	24.33

The molecular weight, by depression of the freezing point of benzene was found to be 991.3, 1053.0, and 997.2.

$(C_{29}H_{52}O_8)_2$ requires 1056.

The samples used in the above combustions were part of the yield of one particularly clean oxidation.

CO_2 evolved during the Oxidation.

Accurate estimation of the CO_2 evolved during the oxidation was difficult since the evolution was slow and lasted for several days, and the gas was contaminated with the vapours of $CHCl_3$ and CH_3COOH from the warm solution.

Experiment revealed that a dilute solution of 5 gm. caoutchouc 175 cc. $CHCl_3$, and 115 cc. CH_3COOH, if heated to 70^o, evolved all the CO_2 in the space of 8-9 hours.

A solution was therefore prepared, using 5 gm. of carefully extracted and dried caoutchouc. The solution was heated till the first bubbles of gas appeared and was then cooled on ice and left overnight in the ice chest. On the following day it was again heated to $70^oC.$, and a current of air was drawn through a soda lime tower into the flask, and then through the condenser to two absorption flasks containing a saturated solution of $Ba(OH)_2$.

When/

When evolution of the gas had ceased, the $BaCO_3$ was filtered, washed, dissolved in HCl, and precipitated as the sulphate.

5 gm. rubber gave 2.0701 gm. $BaSO_4$

∴ Carbon obtained as CO_2 = 2.128% of rubber.

1 carbon per C_5H_8 = 17.65% oxidised

∴ CO_2 is equivalent to 1 carbon per $(C_5H_8)_8$ - $(C_5H_8)_9$.

Derivatives.

As the oxidation product had no acid or ketonic properties, and exhibited the solubility usually associated with an alcohol or glycol, the preparation of the following characteristic derivatives was attempted:-

Nitrobenzoate. Ten grams of the product was dissolved in about 100 gm. pyridine and, to the cold solution, 3 gm. nitrobenzoyl chloride was slowly added. After standing for several days, the solution was poured into water and the pyridine neutralised with dilute H_2SO_4. The product was obtained as a yellow pasty mass, and was separated by filtration. On washing with dilute H_2SO_4 and water, this gradually assumed a granular form. The excess of nitrobenzoic acid was removed by leaving the product in contact with very dilute Na_2CO_3 till all action had ceased. After further washing and drying at the filter pump, the product was repeatedly extracted with ether, in which it was rather sparingly soluble. This effected a partial separation from the resin produced by the reaction, and, on evaporation of the ether, the/

the product was obtained as a brown vitreous mass. Attempts to crystallise it from various solvents failed. During earlier experiments small quantities of crystals separated during the spontaneous evaporation of the ether. These were obtained in an impure condition by extraction with petroleum ether. However, when a sufficient quantity had been collected it was identified as nitrobenzoic acid, M.P. 237°, which the Na_2CO_3 had failed to extract from the pasty precipitate. In later experiments this precipitate was thoroughly dried and pulverised before being treated with Na_2CO_3.

The vitreous mass was extremely soluble in all organic solvents except CS_2 and ether. Repeated extraction with ether left a proportion of the resin behind, but no definite separation could be obtained, and portions submitted to analysis showed a nitrogen content varying from about .5% to nearly 4%. As the product differed in solubility from the original alcohol, it was obvious that esterifaction had taken place to a certain extent, indicating the presence of a primary or secondary alcohol group in the original oxidation product.

Phenylurethane. Two grams of the alcohol, dissolved in dry benzene, was heated with one molecular proportion of phenyl isocyanate in a flask protected by a $CaCl_2$ tube. No resinification occurred even after 10 hours' heating. The benzene was then distilled off and the residue dissolved in ethyl/

ethyl acetate. During the spontaneous evaporation of this solvent a crop of colourless crystals was obtained. These were separated by filtration at the pump and, on recrystallisation from ethyl acetate, were identified as diphenyl urea. MP238°. The syrupy residue closely resembled the original alcohol in its behaviour with solvents. It was, therefore, thoroughly extracted with warm ether in which it was insoluble, dissolved in benzene and precipitated with an excess of petroleum ether. The product, after drying in vacuo, was obtained as a light yellow powder. On fusing with Na, and testing with $FeSO_4$ and $FeCl_3$ this powder was proved to contain no nitrogen.

Acid Phthalate. The preparation of this derivative was attempted by a slight modification of the method of Tiemann and Krüger(Ber.29,I.901). Four grams of the alcohol dissolved in dry benzene was treated with an excess of Na. The solution required gentle warming to start the reaction which then proceeded slowly for several days. The Na derivative of the alcohol settled out as a brownish paste mixed with a certain amount of resin, and the benzene solution became dark in colour. The benzene solution was decanted and the Na salt, suspended in fresh benzene, was treated with 2 gm. phthalic anhydride and allowed to stand for several days at room temperature. The solution was then shaken with water and, after repeated extraction with benzene, the Na salt was obtained as a soap floating on

the/

the aqueous layer, the latter having a distinct red tinge. On acidification a certain amount of resin was precipitated from the aqueous solution. The acid liquid was extracted with $CHCl_3$, and on removal of this solvent by distillation a brown syrup was obtained. Attempts to obtain this in crystalline form failed, and, as it was obviously contaminated with resin formed by the action of the caustic solution on the original alcohol, it was not further examined.

Methylation. The sodium derivative of the alcohol, prepared as above, was suspended in dry benzene and gently warmed under reflux with dimethyl sulphate for several hours. The solution was then poured into water to decompose the excess methyl sulphate, and the product was extracted with benzene. On drying and distilling off the solvent a very dark coloured syrup was obtained. This was completely soluble in most organic solvents, but repeated extraction with ether effected a partial separation from the resin. The final product, however, was still highly coloured, amorphous and unsuitable for analytical purposes.

The Aldehyde.

As the alcohol had failed to yield a suitable derivative which could be definitely purified, attention was turned to preparing from the alcohol, the corresponding aldehyde or ketone. The oxidising action of chromium trioxide dissolved in/

in glacial acetic acid is of a selective character, tending chiefly to oxidise an alcohol to the aldehyde or ketone, the latter product only undergoing further oxidation if an excess of the reagent still remains. To obtain a good yield, therefore, by this reaction, requires accurate determination of the requisite amount of CrO_3.

In the present case, the size and character of the alcohol molecule were unknown, combustions having merely fixed the empirical formula as roughly $C_{10}H_{18}O_3$. In the initial preparations of the aldehyde, therefore, sufficient CrO_3 was used to furnish 1 atom of oxygen to each $C_{10}H_{18}O_3$. In succeeding experiments this quantity was varied and rough estimates made of the respective yields. It was found that decreasing the quantity of CrO_3 resulted in an increased yield of aldehyde. After the aldehyde had been characterised, the theoretical quantity of CrO_3 was used with excellent results; the quantities given below are those used in the most recent preparations.

A solution of 10 gm. of the alcohol in 80 gm. glacial acetic acid was cooled in a freezing mixture. Owing to the colloidal nature of the alcohol, the depression of the freezing point of this concentrated solution was so small that a quantity of water had to be added to prevent solidification. A well cooled solution of 1.3 gm. CrO_3 in 30-40 cc. CH_3COOH was then added in quantities of 2-3 cc., with vigorous agitation after each addition. It had been found, when performing the reaction

at/

at ordinary room temperature, that considerable local oxidation took place before the solutions could be properly mixed, but with the cold solutions, the red colour of the CrO_3 was still undiminished when the addition and mixing was completed.

On allowing the solution to attain room temperature, the oxidation proceeded smoothly and was complete in a few hours. No CO_2 was evolved during the reaction. The solution was poured into about 200 cc. water and the acid almost neutralised by a strong solution of Na_2CO_3. Complete neutralisation of the acid was found to be inadvisable, as it resulted in a gelatinous precipitate of Cr_2O_3 which hindered extraction with ether.

During the neutralisation, the greater portion of the product separated as a white paste. This was removed and dissolved in ether. The aqueous solution was then exhaustively extracted with ether, in which the product was not readily soluble. During the earlier preparations especially, quantities of a product were obtained, which defied extraction with ether. It took the form of a thick greenish soap and, when separated by filtration and dried, it burned with a smoky flame and left a small residue Cr_2O_3. It was decomposed by warm acids to give a green solution and a small clot of resinous matter, and was probably the chromium salt of an acid formed during the oxidation.

The ethereal solution of the product, after washing with water, and drying over anhydrous Na_2SO_4, had that greenish tinge associated with solutions of terpene aldehydes. On removal of the solvent the product was obtained as a clear greenish/

greenish-yellow syrup with a faint pleasant odour, which became more noticeable in alcoholic solution.

A dilute solution in alcohol yielded a mirror with ammoniacal silver oxide and reduced Fehling's solution. This syrup was not volatile in steam, decomposed on distilling under reduced pressure, and, when burned, emitted the characteristic odour of burning caoutchouc. It was moderately soluble in alcohol and benzene, rather sparingly so in ether and insoluble in petroleum ether. Attempts to crystallise it from various solvents and mixtures were unsuccessful. Its properties, therefore, were those of an aldehyde of high molecular weight.

A quantity of the aldehyde, diluted with sufficient ether to give a mobile liquid, was left in contact with a saturated solution of sodium bisulphite for some time. The mixture was frequently agitated, and gradually small crystals were observed to form at the junction of the two layers, the ethereal solution at the same time becoming less viscous. At the end of a fortnight a small quantity of these crystals had been collected. They were removed by filtration and washed with alcohol and ether. On decomposing this bisulphite compound with a strong solution of Na_2CO_3, and extracting with ether, a small quantity of the aldehyde was obtained. The bisulphite solution, after thorough extraction with ether to remove the unattacked aldehyde, was decomposed with solid Na_2CO_3, and again extracted with ether. This yielded a much larger quantity of the aldehyde/

aldehyde, indicating that the bisulphite compound is moderately soluble in the saturated solution of $NaHSO_3$.

As a means of purifying the aldehyde, however, this method was not successful owing to the time required, a heavy and unexplained loss of the aldehyde during the process, and the fact that the largest yield, which was obtained from the decomposed solution, was of doubtful purity.

On treatment in alcoholic solution with semicarbazide acetate, with subsequent precipitation of the product by water, a brownish syrup was obtained with properties differing considerably from the original body. This syrup was extremely soluble in alcohol, both ethyl and methyl, and seemed to be quite insoluble in ether and benzene.

The Semicarbazone.

Five grams of the aldehyde, dissolved in ethyl alcohol, was treated with an excess (2.5 gm.) of semi-carbazide hydrochloride, and the requisite amount of potassium acetate, dissolved in a small quantity of water. On standing, the solution deposited a quantity of KCl and the original greenish tinge changed to a light yellow. No other change being noticed after five days, water was cautiously added to the solution. A considerable addition was necessary before a white curdy precipitate appeared. This precipitate gradually settled and assumed the form of a brownish syrup, the change being apparently due to the presence of the diluted alcohol. The original

form/

form of the precipitate being a desirable one for subsequent handling, an attempt was made to retain ~~it~~ ~~in~~ this form by pouring the reaction solution into a large volume of water saturated with NaCl. This was successful, and the product remained as a thick white curd on the surface of the liquid. On filtering, washing, and drying, it was obtained as a bulky white powder with only a faint odour of the original aldehyde. It was extremely soluble in alcohol and ethyl acetate, insoluble in ether and benzene, and qualitative tests proved that it contained nitrogen. A small quantity was dissolved in alcohol and heated with oxalic acid. The solution was then thrown into water and the excess of acid neutralised. On extraction with ether, the regenerated aldehyde was obtained as a clear yellowish syrup. It was evident, therefore, that this white powder was the semicarbazone of the aldehyde. The semicarbazone could not be crystallised from any solvent or mixture of solvents, slow spontaneous evaporation always resulting in a syrupy residue. Precipitation from solution in alcohol, ethylacetate or acetone, by means of water or ether was also unsuccessful, the original flaky precipitate becoming a smear on the bottom of the flask in the course of afew minutes, even in an ice-cold solution. Precipitation, by throwing the alcoholic solution into water, did not eliminate the unattacked aldehyde or non-aldehyde bodies in the solution, as was proved by the fact that the white powder, on exposure to the air, acquired a pink colour due/

due to the oxidation of these bodies.

Finally the following procedure was adopted. The impurities to be considered were (a) the excess of semicarbazide acetate and KCl, easily soluble in water, (b) a condensation product sometimes obtained from semicarbazide, insoluble in water and cold methyl alcohol, (c) unattacked aldehyde and non-aldehyde products, soluble in both alcohol and ether. The reaction solution containing the semi-carbazone was stirred into a large volume of water, and the precipitate collected and washed. It was redissolved in alcohol and again precipitated, thus ensuring the complete removal of (a). The dry powder was then covered with cold methyl alcohol and solution effected by occasional shaking. After 10 minutes the clear solution was decanted, the undissolved portion being rejected. This eliminated (b) and a proportion of (c). The alcoholic solution was diluted and, after filtration, was distilled down to small bulk. A large excess of sodium-proof ether was then added with vigorous shaking, and the semi-carbazone gradually settled to form a clear, almost colourless syrup. The clear supernatant liquid was then decanted and the product was heated with fresh ether to remove the last traces of (c).

For convenience in handling, the semicarbazone was again dissolved in alcohol, filtered and precipitated by stirring the solution into water. When dry it took the form of a white odourless powder, which did not ~~dissolve~~ discolour on long exposure/

exposure to the air. Specimens were submitted to analysis with the following results:-

(a) .1992 gm. semicarb. gave .4406 gm. CO_2 and .1573 gm. H_2O

(b) .2229 " " " .4904 gm CO_2 and .1754 gm. H_2O.

(c) .3363 gm. " " 20.10 cc. N_2 at 14.5° and 753 mm. N = 7.086%

(d) .3271 gm. " " 19.80 cc. N_2 at 14.5° & 749.3 mm. N = 7.144%

(e) .2287 gm. " " 13.75 cc. N_2 at 22.5° & 758.5 mm. N = 6.988%.

		C	H	N
Found		60.31	8.774	7.086.
		60.01	8.802	7.144
$C_{29}H_{50}O_8N.NH.CONH_2$	requires	60.1	8.849	7.01
$C_{29}H_{48}O_8.N.NH.CONH_2$	requires	60.3	8.543	7.035

Specimens a,b,c,d were selected from different preparations of the semicarbazone; specimen e was used as a test of the method of purification, and consisted of semicarbazone residues obtained during earlier attempts at purification and crystallisation. These residues, which had become highly coloured through long exposure, were mixed, dissolved in methyl alcohol, and purified by the method given above. The nitrogen content was found to agree well with that of the semi-carbazone freshly prepared and purified.

Regeneration of the Aldehyde.

A quantity of the semicarbazone was dissolved in a small volume of ethyl alcohol in a small flask fitted with a capillary pressure/

pressure release. A slight excess over the calculated quantity of oxalic acid was added, and the solution was gently heated for 30 min. On standing and cooling, a portion of the sparingly soluble semicarbazide oxalate separated. The solution was then poured into water and extracted with ether. The excess of oxalic acid was removed by washing the ethereal solution with Na_2CO_3 after which the ethereal solution was dried and the solvent distilled off. The aldehyde remained as a clear yellowish syrup with a faint pleasant odour.

In alcoholic solution, especially if warm, the aldehyde oxidises rapidly and during its preparation from the semicarbazone, precautions are necessary to protect it from spontaneous oxidation.

The state of aggregation of the semicarbazone renders it very resistent to aqueous oxalic acid, and decomposition by this method was unsuccessful.

The Acid.

As the aldehyde on standing gradually dried to a hard vitreous mass, dilution with a solvent was necessary to effect spontaneous oxidation. The best method consisted in dissolving it in ethyl alcohol, placing the solution in an evaporating basin and maintaining it at about 40°, the alcohol being replenished as it evaporated. The solution gradually acquired a dark red colour, and after about 10-12 days' heating the alcohol was allowed to evaporate completely and the product was treated with Na_2CO_3 solution. A considerable quantity of resinous matter remained/

remained undissolved. The pink solution of the sodium salt was filtered and acidified, and the acid was precipitated in a gelatinous form, gradually coagulating to form red clots on the surface of the liquid. Extraction with ether was difficult, as the acid was only sparingly soluble in this medium, and also exhibited a tendency to adhere to the sides of the vessel. An improvement was effected by saturating the solution with NaCl before acidifying, the acid, on precipitation, coagulating to form a scum instead of hard insoluble lumps.

On distillation of the ether the acid remained as a dark red syrup with a pleasant fruity odour. It was almost insoluble in water and benzene, easily soluble in alcohol, acetone and chloroform.

Oxidation of the aldehyde by means of dilute HNO_3 was not very successful. A small quantity of the aldehyde syrup, when heated to 50° with very dilute HNO_3 yielded a light yellow solid which, when dry, became brittle and could be easily powdered. This substance, on boiling with Na_2CO_3, furnished only a small quantity of the acid and the insoluble portion on further treatment with HNO_3 seemed to undergo no change. Better results were obtained by dissolving the aldehyde in CCl_4 and covering the solution with dilute HNO_3. This mixture was maintained at 40-50°C and frequently agitated, CCl_4 being added when necessary. The lower solution gradually became

dark/

dark red, and after about 10 days' heating, was separated and the CCl_4 distilled off. On extraction of the residue with Na_2CO_3, a small quantity of acid was obtained, which in appearance, odour, and solubility resembled that obtained by spontaneous oxidation. Only the latter acid was obtained in quantities sufficient for investigation.

On heating with NH_4OH, a pink solution of the ammonium salt of the acid was obtained. The solution was boiled till neutral and portions were treated with $CaCl_2$, $BaCl_2$, $AgNO_3$, and $(CH_3COO)_2Pb$. Only the latter two yielded insoluble salts, and these were obtained as brown gelatinous precipitates, which had to be filtered at the pump after washing by decantation. The silver salt decomposed slightly while settling from the solution, and quickly on being washed with warm water.

The lead salt seemed stable, and was filtered and thoroughly washed at the pump. On drying in vacuo it was obtained as a dark brown gritty powder. The lead content was determined by treating the salt in a crucible with fuming HNO_3 and conc. H_2SO_4 till a white residue of $PbSO_4$ of constant weight was obtained. Analysis of two different preparations gave:-

.1505 gm. salt gave .0582 gm. $PbSO_4$.

Pb = 26.43%.

.4062 gm. salt gave .1554 gm. $PbSO_4$

Pb = 26.14%.

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THE OXIDATION OF SABINENE WITH CHROMYL CHLORIDE.

BY

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AND

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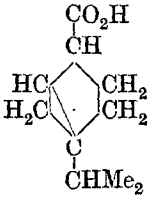
CCCXXVI.—*The Oxidation of Sabinene with Chromyl Chloride.*

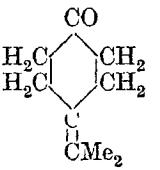
By George Gerald Henderson, John McGregor Robertson, and David Christie Brown.

Previous investigations have shown that a number of the terpenes, both monocyclic and dicyclic, unite additively with chromyl chloride to form solid compounds of the formula $C_{10}H_{16},2CrO_2Cl_2$, which, when decomposed by water, yield mixtures of aldehydes and ketones derived from the corresponding hydrocarbons (Bredt and Jagelki, *Annalen*, 1900, **310**, 112; Henderson and others, T., 1903, **83**, 1299; 1908, **93**, 288; 1911, **99**, 1887). It has now been found that in this respect sabinene resembles other dicyclic terpenes. When a dilute solution of chromyl chloride in carbon disulphide is slowly added to a similar solution of sabinene, care being taken to prevent rise of temperature, a solid separates. This compound is readily decomposed by water, with formation of an insoluble liquid product together with a certain quantity of resinous matter. The principal constituents of the liquid, apart from some indefinite

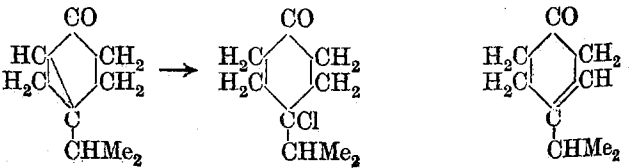
resinous materials, are a saturated *aldehyde*, $C_9H_{15}\cdot CHO$, and an unsaturated ketone, $C_9H_{14}O$, which are present in approximately equal proportions. In addition, a small quantity of an isomeric ketone was separated in the form of its semicarbazone.

The aldehyde, which is a viscous liquid, undergoes spontaneous oxidation on exposure to air. The crystalline *acid*, $C_9H_{15}\cdot CO_2H$, thus produced melts at 175°; it is also obtained when the aldehyde is heated with dilute nitric acid. As the acid is prepared from sabinene by a method similar to that by which camphene is converted into camphenilanic acid, it may be named sabinenilanic acid. Its constitution has not been elucidated as yet, but if it be assumed that the structure of the sabinene nucleus remains unchanged during the process of oxidation, the formula will be (I).

(I.) 

(II.) 

The two ketones were separated by taking advantage of the difference in solubility of their semicarbazones, that of the chief constituent being very sparingly soluble and the other readily soluble in cold alcohol. After several crystallisations, the former semicarbazone showed a constant melting point of 205°. The ketone, $C_9H_{14}O$, liberated from it is a colourless liquid of pleasant odour, which boils at 220° and behaves as an unsaturated compound towards bromine and potassium permanganate. Taking into account the properties of the ketone as well as those of its semicarbazone, there can be little doubt that it is 4-*iso*propylidene-*cyclo*hexanone (II). This ketone was obtained by Perkin (T., 1907, **91**, 1736) as a product of the hydrolysis of ethyl 4-*iso*propylidene-*cyclo*hexanone-2-carboxylate, and also by Wallach (*Annalen*, 1908, **359**, 265) on heating with dimethylaniline the compound (IV) which he had prepared by the action of hydrogen chloride on sabina ketone (III). The melting point of the semicarbazone of our ketone is, however, somewhat higher than that (201°) quoted by these observers.



(III.) (IV.) (V.)

On reduction with sodium and alcohol, the ketone is converted into the secondary alcohol, 4-iso*propylidene*cyclo*hexanol*, C_8H_{14}>CH·OH, a liquid with a pleasant odour which boils at 134°/40 mm. Its p-*nitrobenzoate* is a colourless, crystalline solid, m. p. 63°.

After repeated crystallisations, the melting point of the semicarbazone of the ketone present in small quantity in the original oxidation product was found to be 168—169°, whilst Wallach (*loc. cit.*) gives as 169—170° the melting point of the semicarbazone of 4-*iso*propyl-Δ^3-*cyclo*hexenone (V). This ketone he obtained, together with the isomeric Δ^2-compound as principal product, on heating sabina ketone with 20 per cent. sulphuric acid. The quantity of the semicarbazone of m. p. 169° in our hands was so small that it was not possible to separate and identify the ketone.

It might have been anticipated that sabina ketone would be one of the products of the action of chromyl chloride on sabinene and it is at least possible that this was actually the case, and that the sabina ketone originally formed was caused to undergo intramolecular rearrangement under the influence of the hydrochloric acid which is always liberated along with chromium chloride and a little chromic acid when the additive products, $C_{10}H_{16},2CrO_2Cl_2$, are decomposed by water. If that had been the case, however, one would have expected, in view of Wallach's results, to find 4-*iso*propyl-Δ^2-*cyclo*hexenone in our product, whereas none of this compound could be detected.

Experimental.

Separation and Oxidation of Sabinene.

Sabinene was separated from oil of savin as follows. The oil was distilled in a current of steam for about half an hour, and the oily distillate collected and treated under reflux for some time with sufficient alcoholic sodium hydroxide to hydrolyse the sabinol esters which it contained. After passing in carbon dioxide to neutralise any free alkali, the mixture was distilled in steam, and the distillate collected in two approximately equal fractions. The first of these, which contained practically all the sabinene, was extracted with light petroleum, the extract dried over anhydrous sodium sulphate, the solvent removed, and the residual liquid distilled in a current of dry carbon dioxide. The yield of sabinene (b. p. 163—165°) obtained was nearly 19 per cent. of the weight of the oil of savin.

A 10 per cent. solution of 100 grams (rather more than 2 mols.) of chromyl chloride in carbon disulphide was added, in small quantities at a time and with constant agitation, to a similar solution of 40 grams (1 mol.) of sabinene, both solutions being well cooled with ice-water. During this part of the process, any failure to

keep the solution cool results in much loss by resinification of the sabinene. A precipitate of the solid compound began to separate at once, and was left to settle for a day or two. The liquid was then decanted, and the thin, pasty mixture of the solid compound and carbon disulphide poured, in small quantities at a time, into ice-cold water, with vigorous agitation after each addition. The quantity of carbon disulphide present in the mixture was sufficient to extract most of the oxidation product from the water, and the last traces were recovered by successive extractions with ether and with light petroleum. The solutions were washed with water and dried over anhydrous sodium sulphate, and the solvents removed by distillation. As the residual oxidation product contained a considerable proportion of resinous substances, it was further purified by distillation in steam, an approximately 50 per cent. yield being obtained.

The solid additive compound, $C_{10}H_{16},2CrO_2Cl_2$, is very similar to those obtained from other terpenes. When dry, it is a grey powder, which quickly begins to undergo decomposition when exposed to moist air, and which reacts vigorously with water.

Separation and Oxidation of Sabinenilanaldehyde.

The oxidation product, after steam distillation, was mixed with excess of a freshly prepared saturated solution of sodium hydrogen sulphite, and shaken at intervals for several days. The *bisulphite* compound, which separated slowly in the form of a colourless, finely crystalline solid, was collected and washed with alcohol and with ether. The residual oily liquid recovered from the filtrate and washings was again shaken with sodium hydrogen sulphite, and the process repeated until no further separation of crystals took place. The bisulphite compound was heated with excess of aqueous sodium carbonate, and the liberated aldehyde distilled off in a current of steam, separated from the distillate by means of ether, and purified by distillation.

Sabinenilanaldehyde, $C_9H_{15}\cdot CHO$, is an almost colourless, viscous liquid, which boils at 215—217°, and has the strong, peculiar odour characteristic of such terpene aldehydes. It dissolves easily in the usual organic solvents, and is oxidised to the corresponding acid when exposed to air. The *semicarbazone* of the aldehyde, prepared in the usual manner, separates from methyl alcohol, in which it is freely soluble, in colourless crystals, m. p. 145—146° (Found: N = 20·0. $C_{10}H_{16}O$ requires N = 20·1 per cent.).

Sabinenilanic acid, $C_9H_{15}\cdot CO_2H$, was prepared by spontaneous oxidation of the aldehyde, and also by heating it with dilute nitric acid. It was purified by crystallisation from benzene, from which it separates in small, colourless prisms, m. p. 175—176°. It is

very readily soluble in alcohol or ether, and sparingly soluble in water or cold benzene. Towards bromine or potassium permanganate, it behaves as a saturated compound. The *sodium*, *calcium*, and *barium* salts are readily soluble in water, the *silver* salt almost insoluble (Found: C = 71·3; H = 9·7. $C_{10}H_{16}O_2$ requires C = 71·4; H = 9·5 per cent.).

Separation and Reduction of 4-iso*Propylidene*cyclo*hexanone.* The mixed ketones which remained after removal of the aldehyde from the original oxidation product were converted into semicarbazones in the usual manner. The mixture of semicarbazones was dissolved in boiling alcohol and on cooling the bulk crystallised, but a small portion remained in solution and was precipitated by addition of water after removal of the crop of crystals. By repetition of this process, we obtained a semicarbazone which melted sharply at 205°, and a small quantity of a second semicarbazone with a melting point of 168—169°. The ketone, 4-*iso*propylidene-*cyclo*hexanone, $C_9H_{14}O$, was prepared by decomposing the semicarbazone of m. p. 205° with the calculated quantity of oxalic acid, distilling the mixture in a current of steam, and extracting the ketone from the distillate with ether. It is a colourless liquid of a pleasant odour which distils at 220° without decomposition, and as an unsaturated compound at once reacts with bromine and with potassium permanganate. It is almost insoluble in water, and readily soluble in alcohol or ether. Its composition was determined by analysis of the semicarbazone (Found: C = 61·9; H = 8·7; N = 21·7. Calc., C = 61·5; H = 8·8; N = 21·5 per cent.).

The corresponding *alcohol*, 4-iso*propylidene*cyclo*hexanol*, $C_8H_{14}>CH\cdot OH$, was prepared by addition of sodium in excess to a methyl-alcoholic solution of the ketone, and subsequent treatment with water, extraction with ether, and distillation of the crude product under diminished pressure. The alcohol was thus obtained as a colourless, viscous liquid with an odour somewhat like that of menthol. It boils at 134°/40 mm. and is sparingly soluble in water, but dissolves easily in alcohol or ether. When treated, in pyridine solution, with *p*-nitrobenzoyl chloride, it yields a p-*nitrobenzoate*, which crystallises from alcohol in small, colourless prisms, m. p. 63°.

We are indebted to the Department of Scientific and Industrial Research for a grant which enabled one of us (J. M. R.) to take part in this work, and to the Carnegie Trust for a grant which defrayed part of the expense.

UNIVERSITY OF GLASGOW. [*Received, November 7th*, 1922.]

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NOTES.

The Oxidation of Sabinene with Chromyl Chloride. A Correction.

By G. G. Henderson and J. M. Robertson.

In a paper on "The Oxidation of Sabinene with Chromyl Chloride" (Henderson, Robertson, and Brown, T., 1922, **121**, 2717), the suggestion was made that one of the ketones obtained when the solid product of the action of chromyl chloride on sabinene is decomposed with water is 4-*iso*propylidene*cyclo*hexanone. Dr. Henry has kindly pointed out to us that the semicarbazones of our ketone and of *p*-tolyl methyl ketone have the same melting point, and that he has observed no depression in the melting point

of a mixture of the two. We have consequently examined a fresh specimen of the ketone, prepared from the purified semicarbazone, and have found that it is not unsaturated, as our original tests appeared to indicate, but is in fact *p*-tolyl methyl ketone. It follows that the alcohol which we obtained by the reduction of the ketone is methyl-*p*-tolylcarbinol.

Errera has shown (*Gazzetta*, 1891, **21**, 96) that *p*-tolyl methyl ketone is produced by oxidising cymene with chromyl chloride, and the formation of this ketone from sabinene, although unexpected, is not difficult to understand. It is evident that whilst part of the sabinene unites with chromyl chloride to form the compound $C_{10}H_{16},2CrO_2Cl_2$, another part is converted by the oxidising action of the reagent into cymene, and this in turn combines with chromyl chloride to form the solid $C_{10}H_{14},2CrO_2Cl_2$, which yields *p*-tolyl methyl ketone on treatment with water. In this connexion, it may be recalled that this ketone is also obtained by the action of chromyl chloride on both limonene and terpinene, these terpenes likewise undergoing partial oxidation to cymene (Henderson and Cameron, T., 1909, **95**, 969).—[*Received, January* 31*st*, 1924.]

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THE ACTION OF SULPHUR MONOCHLORIDE ON CAMPHENE.

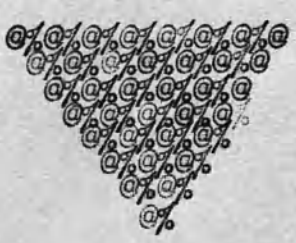
- by -

J. MacGregor Robertson, B.Sc., A.I.C.

GLASGOW UNIVERSITY.

26th September.

- 1922 -



ABSTRACT.

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The object of the experiment was to verify the existence and if possible determine the position of the $= CH_2$ group in the present accepted formula of camphene. The method was to utilise the reaction of Guthrie (Quart.Jour.Chem.Soc.1860. 12.116) between ethylenic compounds and sulphur monochloride. It was hoped to attain a compound of the formula

$$Cl \cdot C_9H_{14} \cdot CH_2 \cdot S \cdot CH_2 \cdot C_9H_{14}Cl.$$

This was not realised as the reaction even in a freezing mixture was too vigorous and resulted in resinification. By arresting the reaction before it had completed its course, small quantities of an unsaturated chloro compound were obtained. This when purified, was a white crystalline powder, melting point 110° (not sharp). On analysis it approximated to the formula $C_{10}H_{15}Cl$. It is a monochloro camphene but does not correspond to any previously described.

This was the only definite product of the reaction, the rest being resins, and decomposition products from vacuum distillation.

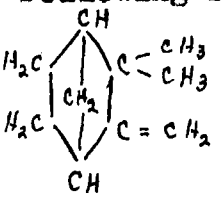
When it was evident that this research would throw no further light on the camphene problem, the work was discontinued, and a more promising problem started by another student was carried to a conclusion.

THE ACTION OF SULPHUR MONOCHLORIDE ON CAMPHENE.

----------oOo----------

The structure of camphene has led to considerable specula-
on and even at present the subject is somewhat unsatisfactory.
s mode of preparation alone shows that in all cases considerable
lecular rearrangement occurs during the formation of the
bstance. Camphene may be prepared therefore from borneol
the action of potassium bisulphate at 200°; from isoborneol
the action of Zn Cl_2 or dilute H_2SO_4; from pinene hydrochloride
isobornyl chloride) and sodium acetate in glacial acetic acid at 200°;
rom bornyl chloride by the action of aniline, pyridine etc.
amphene may thus be prepared from either borneol or isoborneol
r their derivatives. Furthermore camphene in the presence of
cids usually gives esters of isoborneol.

Its behaviour on oxidation has if possible tended to make the position worse. However the series of oxidation products obtained using $KMNO_4$ (A.340.17) point fairly definitely to the formula recognised at present. The products obtained started with a camphene glycol MP200° and finished with isopropylcyclopentane carboxylic acid. These point to the following formula for camphene first proposed by G. Wagner.



It was with a view to verifying the $= CH_2$ side chain that this experiment was started.

Guthrie/

Guthrie (loc.cit.) found that on passing ethylene through ulphur monochloride, a vesicant compound was obtained to which e assigned the formula $C_4H_8Cl_2S_2$. This was a matter of onsiderable contention till in 1917 Gibson and Pope (JCS.1920. rans.271) put the matter on a sound footing during the preparation of toxic gases for war purposes. They found that ethylene passed into S_2Cl_2 at any temperature up to 70° gave an almost quantitative yield of BB[1] chlorethyl sulphide

$$Cl\,CH_2.\,CH_2.\,S.CH_2.CH_2Cl.$$

Working on these lines it was hoped to obtain with camphene a compound of the type

$$C_9H_{14}Cl.CH_2.S.CH_2.C_9H_{14}Cl,$$

thereby verifying the ethenoid linkage in the molecule. The reaction was tried in carbon tetrachloride solution at various concentrations and temperatures. In all cases it was found that the final product of the reaction was a resin, the time taken to reach this stage depending on the concentration and temperature.

By performing the reaction in a freezing mixture and arresting it by destroying the S_2Cl_2 with water it was possible to obtain by crystallisation or vacuum distillation, a product which contained chlorine but no sulphur. This compound, of which only a small quantity was obtained, was purified as far as possible and analysed. The chlorine content was very low

but/

but approximated to that of $C_{10}H_{15}Cl$. The compound seemed to be a monochloro camphene but does not resemble any at present known. It was moderately soluble in methyl alcohol, and extremely so in ether, acetone and all hydrocarbon solvents. It was unstable, becoming resinous on long standing. It was extremely difficult to separate this product from the camphene present when the reaction was arrested. The melting point after repeated recrystallisation from methyl alcohol, rose to 108-110° at which it remained. It distilled at about 110°/15 mm.

The other products of the reaction were a yellow resin containing much sulphur in suspension, and a dark red oil obtained by distillation in vacuo. The resinous product would not crystallise and was not examined. The dark red oil was obtained at 120°/15 mm. with much decomposition. On standing even for a day or two it became viscous and resinous. It could not be purified as further distillation in vacuo merely caused more decomposition with the production of tarry residues.

As it was now obvious that this work would throw no sidelight on the camphene problem, the research was abandoned and a more promising line of experiment taken up.

----------oOo----------

EXPERIMENTAL.

Preparation of Camphene.

----------oOo----------

The camphene was prepared by the method of Wallach by acting on Isobornyl chloride with fused sodium acetate in glacial acetic acid. 40 gm. Isobornyl Chloride, 40 gm. fused sodium acetate, and 80 gm. glacial acetic acid were heated under reflux for 10 hours. The contents of the flask solidified on cooling. The solid was melted, removed to another flask and steam-distilled. The camphene came over easily at first but towards the end tended to choke the condenser. The distillate, when cool, solidified and was extracted with ether, washed with Na_2CO_3 to remove acetic acid. On distilling off the ether, a white solid is obtained. This however was found to contain a large amount of Cl, showing the presence of unchanged pinene hydrochloride. It was again treated as before but the final product still showed the presence of chlorine.

The unchanged pinene hydrochloride was successfully separated during the steam distillation by cutting down the water supply to the condenser till the distillate was almost at the boiling point. The camphene, on account of its high volatility and low melting point, distilled over first and did not solidify even in the receiver; the pinene hydrochloride, on the other hand, showed its presence at once by solidifying in the lower part of the condenser. As soon as this occurred

the/

the receiver was changed and the pinene hydrochloride obtained was subjected to a further treatment with sodium acetate.

The camphene was, as before, extracted with ether, washed with Na_2CO_3, and dried over $CaCl_2$. The ether was distilled off and the camphene obtained as a white solid, M.P.53-54°C. B.P.154°. It was free from chlorine.

PURIFICATION OF THE SULPHUR MONOCHLORIDE.

The S_2Cl_2 was the ordinary commercial product. This contains as impurities, sulphur dichloride, SCl_2, and metallic salts, chiefly iron. The SCl_2 causes direct chlorination, whilst the Fe salts cause chlorination by catalysis. These impurities were removed by repeated distillation of the liquid with the addition of small quantities of sulphur. The pure liquid boiled at 136.5 - 137.5°C and was preserved in a tightly stoppered glass vessel, with the addition of about 2.5% sulphur.

THE REACTION.

5 gm.(1 mol.) camphene was dissolved in the smallest quantity of $C Cl_4$. 5 gm S_2Cl_2 was then added slowly. The solution became very hot and gradually changed from orange yellow to dark red. HCl was evolved showing that a certain amount of substitution was ta ing place. After standing overnight it was found that HCl was still being evolved. A

portion/

portion of the liquid was distilled. After removal of the C Cl_4, a fraction distilled at 160°-170° with considerable decomposition. The distillate solidified on cooling to a thick brown oil. This was easily soluble in chloroform and on gentle evaporation a few minute brown crystals were obtained. The quantity was too small to purify, the melting point being 103-107°C. Another portion of the solution was concentrated by evaporation in vacuo. A thick sticky oil was obtained, which on being dissolved in ether gave a heavy precipitate of sulphur. The etherial solution was evaporated and a brown oil obtained which grew very viscous but did not crystallise.

A similar reaction was carried out using 10 gm.(2 mols.) camphene to 5 gm.(1 mol.) S_2Cl_2. Just sufficient C Cl_4 was used to dissolve the camphene. The solution became warm as before and gradually turned dark red. The C Cl_4 was distilled off and the thick brown product dissolved in ether. Sulphur was precipitated and on filtering and evaporating, a dark brown resinous product was again obtained. This, on standing, continued to evolve HCl and did not crystallise. A portion of the original solution was distilled in vacuo. After removal of the CCl_4 at 20°C/15 mm., some camphene came over at 50°/15 mm. and finally a dark red oil distilled at 120°/15 mm. with great decomposition. There was also a large tarry residue. This oil could not be purified as at each subsequent distillation, more/

more decomposition occurred and further resinous residues were obtained. The oil, mobile at first, became thick and gummy on standing. It had a strong smell resembling burnt rubber.

A reaction was tried using 2 mols. camphene to 1 mol. S_2Cl_2. The solution was heated on the waterbath. It was found that at about 80°C. HCl was evolved in quantities, the evolution becoming very copious as the temperature was raised; the solution turned black very rapidly. On evaporation of the $C Cl_4$, a very dark resin was obtained. This would not crystallise from any solvent, and distillation in vacuo only produced a small amount of unchanged camphene.

From the above reactions it was evident that the reaction normally results in the resinification of the terpene. This is accelerated by (1) heat (2) concentration of the solution, (3) failure to remove the excess of S_2Cl_2 once the required point of the reaction has been reached.

Another reaction was therefore tried, this time in dilute solution and in the cold. A 10% solution of camphene (2 mols.) in $C Cl_4$ was made. This was cooled in a freezing mixture and to it was added very slowly a well cooled 10% solution of S_2Cl_2 in $C Cl_4$. The solution was well shaken during the addition of the S_2Cl_2 to prevent local overheating. It was kept on ice for several days and the colour changes noted. These changes were:-

Initial - light green
deep green
green-yellow
yellow
amber
red
Final - black.

number of small solutions were made on the above lines and arrested the colour stages mentioned and the products were examined. The procedure followed in each case was the same and ensured that no heating occurred till the excess of S_2Cl_2 was destroyed. The products could then be left for some time without fear of decomposition setting in. The method was as follows:- when the desired stage had been reached, the solution was removed to another flask and the CCl_4 removed by evaporation in a stream of cool dry air drawn through by a pump. This evaporation kept the temperature down to freezing point. When evaporation was complete the product was quickly dissolved in a large volume of light petroleum and shaken well with ice cold water. This decomposed the excess S_2Cl_2 and a copious precipitate of sulphur was obtained. The water and petroleum solution was then drained off and the sulphur removed to a beaker where it was covered with light petroleum and squeezed till everything had been extracted from it. The petroleum solution was separated from water, dried over $CaCl_2$, and the petroleum distilled off in vacuo. This could be done at a temperature of about 20-25°C. The product so obtained was free from S_2Cl_2 and could be safely handled without further decomposition or evolution of HCL.

In each case the product was divided in two, one half being

placed/

laced in a vacuum ~~desiccator~~ desiccator to crystallise and the other part ing distilled in vacuo. The products found at each stage of he reaction are given below:-

age.	Portion left to crystallise.	Portion vacuum distilled.
eep green.	Obtained camphene (MP53°) and small portion yellow resin.	Obtained camphene and dark red oil at 120°/15mm. Considerable charring.
reen yellow.	As above. Camphene fraction was smaller.	Camphene distilled at 50°/ 15 mm. yellow oil distilled 100-110°. Solidified to yellowish crystals M.P. 100-103°. Decomposition products.
yellow.	As above. Crystallisation slow and crystals difficult to separate from viscous oil.	As above.
Amber.	Crystallised with difficulty giving yellowish crystals M.P.80°. On purification M.P.95°.	Gave larger yield of crystals of M.P. 100-103°. Large yield of dark red oil. Much decomposition.
Red.	Smaller yield of crystals as above. Yellow viscous oil which would not crystallise.	As above.
Black.	Resin which would not crystallise.	Gave dark red viscous oil with much charring.

It was therefore evident that a definite product could be obtained if the reaction were stopped before the solution became red in olour. It was found that a better yield was obtained by crystallising the product in preference to vacuum distillation which was very wasteful with the small quantities used.

THE CRYSTALLINE PRODUCT.

After arresting the reaction by washing with water, the dried petroleum solution was distilled in vacuo. When the temperature reached about 22°/15 mm. the distillation was stopped and the amber coloured oil was removed to a vacuum desiccator. On standing the oil became viscous and crystals began to appear. At the end of 10 days or more the product was filtered at the pump. This operation took about 10 hours as the oily portion was very viscous. The crystals were of a yellowish colour. They were extremely soluble in benzene and light petroleum and therefore these solvents were not of much use in purifying. Methyl alcohol was found to be the best medium as the substance was readily soluble in hot and sparingly so in cold. A preliminary purification from benzene was found to be necessary, as the substance otherwise tended to settle out of the alcohol in the form of an oil. This trouble was continually met with in dealing with the first crystallisation of this product. One useful method of avoiding it consisted in spreading the crude crystalline product thinly over porous pot and allowing to stand in vacuo till absolutely dry. This frequently took a fortnight to complete. On dissolving the crude product in hot alcohol a precipitate of sulphur was obtained. This persisted to a smaller extent in the next two crystallisations. The pure product crystallised in white feathery tufts, closely resembling the form of/

of camphene crystals obtained from methyl alcohol. During purification the melting point rose from about 80°-90°C. to 108°-110° at which it remained. The product was white, had a faint odour like camphor, and became tough on standing, like camphene or pinene hydrochloride. On long standing, two months or so, even in a tightly corked flask it became slightly resinous and the melting point dropped. It behaved as an unsaturated body towards Br_2 and $KMnO_4$. It was found to contain C., H, and Cl No S. was obtained either by fusing with Na and testing with sodium nitroprusside or by careful fusion with sodium peroxide and testing with $BaCl_2$. The substance therefore seemed to be a chlorocamphene.

The chlorine content, estimated by the method of Carius gave the following:-

(1) ·2066 gm. gave ·1360 gm.AgCl Cl = 16·29%

(2) ·1408 gm. gave ·0907 gm. AgCl Cl = 15.94%

(3) ·2180 gm. gave ·1553 gm. AgCl Cl = 17.62%

$C_{10}H_{15}Cl$ requires Cl = 21.31%

$C_{10}H_{14}Cl_2$ " Cl = 34.63%.

The substance thus seems to be a monochlorocamphene, containing a certain amount of camphene as an impurity. After estimations (1) and (2) when it was evident that the substance was still impure/

impure it was again recrystalised from methyl alcohol and placed for several days in a vacuum in the hope that the volatile camphene would thus be removed. It was again recrystallised. The melting point still remained at 108°-110°. Estimation (3) was then performed and it will be seen that only a small part of the impurity was eliminated by this treatment.

To find the effect of camphene in the product, equal weights of camphene and the chloro compound were mixed and dissolved in hot methyl alcohol. The melting point of the first crop was about 75°C. Several purifications were necessary before 100° was reached. Incidentally the tendency to separate out from the alcohol as an oil was most marked in the early stages.

It is thus evident that the product of the reaction is a chlorocamphene. $C_{10}H_{15}Cl$. It does not compate with any of the chlorocamphenes already known.

THE VACUUM DISTILLED PRODUCT.

On distilling the crude yellow oil at 15 m.m. pressure, the first product obtained was camphene which appeared at about 50°-60°C. At 100-110°C. a yellow oil came over which solidified in the condenser. Decomposition of the contents of the flask also set in about the same time. On removing the solid and continuing the distillation, the dark red oil already mentioned was obtained.

The/

The solid product was dissolved in benzene, and on evaporation was obtained in a slightly purer condition. It was then purified as before by repeated crystallisation from methyl alcohol. The tendency to form an oil was marked in the early stages. The melting point rose till 108° was reached at which it remained stationary. A mixture of this product and the one obtained by ordinary crystallisation was recrystallised from methyl alcohol and the melting point of the mixture was still 108-110°C. The substance obtained by distillation under reduced pressure is therefore identical with that described above. Owing to the difference in the boiling points of camphene and the chlorocamphene under reduced pressure i.e. 50-60° and 100-110°, a fractional distillation in vacuo might have effected a complete separation, but the quantity at our disposal was too small to permit of this.

THE VISCOUS OIL.

The crude product from which the crystals were obtained, contained a large amount of a yellow viscous oil which was removed from the crystals by prolonged filtration at the pump. A small second crop of crystals was usually obtained from the oil but a large portion always failed to crystallise. This was examined in various ways. It contained a large amount of sulphur which was precipitated from such solvents as light petroleum and alcohol. On distilling under diminished pressure

it/

it gave small quantities of camphene and the chlorocamphene with much decomposition and charring. The contents of the flask after distilling often resembled partially burned rubber and on burning on a spatula produced much SO_2.

The substance is probably the resinified portion of the terpene, holding in solution, or suspension, camphene, chlorocamphene and a large quantity of finely divided sulphur.

At this point it was evident that the object of the research, which was to obtain a compound of the structure $(\alpha . C_9H_{14} . CH_2)_2 S$. and so confirm the $= CH_2$ group in the camphene molecule, would not be realised. The chlorocamphene obtained, whilst interesting in that it does not correspond to any already known, throws no additional light on the constitution of this very reactive molecule, and merely adds one more to the already large list of camphene substitution compounds.

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